SUNLIGHT AND ORGANIC DYES AS A GREENER APPROACH TO PHOTOCHEMICAL REACTIONS AND DEGRADATION OF PHENOL IN WATER

BY

AHMED ABDI HASSAN

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

ENVIRONMENTAL SCIENCE

MAY 2015

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **Ahmed Abdi Hassan** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN ENVIRONMENTAL SCIENCE.**

Dr. Basheer Chanbasha
(Advisor)

Dr. Abdulaziz Al-Shaibani
Department Chairman

Professor Abdulrahman Al-Arfaj
(Member)

Dr. Salam A. Zummo
Dean of Graduate Studies

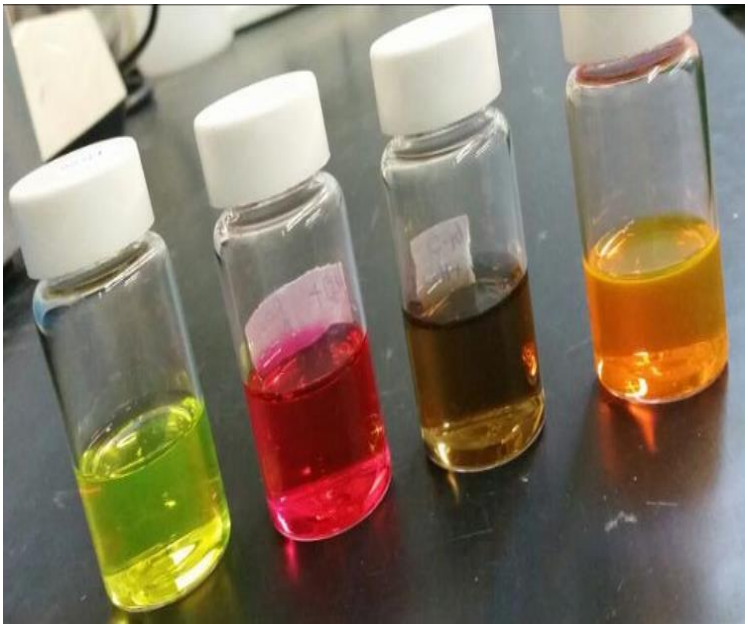
26/5/2015

Dr. Bassam Shafiq Tawabini
(Member)

28/5/15

Date

DEDICATED TO MY BELOVED PARENTS, WIFE, BROTHERS AND SISTERS



"Research is formalized curiosity. It is poking and prying with a purpose."

-Zora Neale Hurston

ACKNOWLEDGMENTS

I would like to take this opportunity to express my special sincere and profound appreciation to my advisor Dr. Basheer Chanbasha, you have been incredible, simple, hardworking, readily available and a real mentor for me. Your advice on both research as well as on my career have been priceless and exceeded my expectations. I would also like to take this opportunity to thank my committee members, Dr. Bassam Tawabini and Professor Abdulrahman Al-Arfaj for serving as my committee members in their tight schedule. I also want to thank them for your brilliant comments, inputs, suggestions, and advices, thanks to them again. I would especially like to extend my word of thanks to National Science, Technology and Innovation Plan (NSTIP) for their financial support of this research project under research grant no13-ENE277-04.

I am grateful to King Fahd University of Petroleum & Minerals for the opportunity to pursue my master's degree. I am especially thankful to all staffs, students and lecturers in the Earth Sciences Department, for the support and inspiration I received throughout the period of my study particularly from the chairman Dr. Abdulaziz Al-Shaibani who was my academic advisor. The contributions of the glass blower and the lab technicians to this work was precious. I would also like to thank all my friends who supported me in this work.

A special thanks to my all family members. Words cannot express how grateful I am to my father, brothers and sisters for all of the sacrifices they have made on my behalf. Their prayers was what brought me all this far. At the end I would like to express appreciation to my beloved wife Basra Bare who spent sleepless nights in my absence and was always on my support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

RB	:	Rose Bengal
O.D	:	Organic Dye
U.V	:	Ultraviolet
SET	:	Single Electron Transfer
NMR	:	Nuclear Magnetic Resonance
HPLC	:	High Performance Liquid Chromatography
UHPLC	:	Ultra High Performance Liquid Chromatography
LCMS	:	Liquid Chromatography Mass Spectrometer
FTIR	:	Fourier Transform Infrared Spectroscopy
XRD	:	X-Ray Diffraction
GO	:	Graphene Oxide
DCM	:	Dichloromethane
ACN	:	Acetonitrile
EU	:	European Union
PPM	:	Parts Per Million
USEPA	:	United State Environmental Protection Agency
WHO	:	World Health Organization

ABSTRACT

Full Name : Ahmed Abdi Hassan

Thesis Title : Sunlight and Organic Dyes as a Greener Approach to Photochemical Reactions and Degradation of Phenol in Water

Major Field : Environmental Science

Date of Degree : May 2015

In this work we have designed and developed a new reactions utilizing sunlight in the presence of organic dyes photocatalyst *via* flow microreactor. We have successfully synthesized several organic compounds in a flow capillary reactor and degraded phenol in water and also developed and optimized the reaction conditions. Organic dye photocatalyzed α-Functionalization of tertiary amines, α-oxyamination of 1,3-dicarbonyl compounds and degradation of phenol in water were used as a model to develop completely 'greener approach' of photochemical synthesis and degradation, taking into account all steps of the processes. Utilization of non-concentrated solar irradiation conditions of Saudi Arabia was demonstrated in King Fahd University of Petroleum and Minerals. In almost all the experiments conducted in this study, the flow reactor gave yield higher than 64% and maximum phenol removal of 86.6% from contaminated water.

ملخص الرسالة

الاسم الكامل : أحمد حسن عبدي

عنوان الرسالة : أشعة الشمس والأصباغ العضوية كنهج خضرة إلى التفاعلات الضوئية وتدهور الفينول في المياه

التخصص : العلوم البيئية

تاريخ الدرجة العلمية :مايو 2015

في هذا العمل الذي قمنا بتصميم وتطوير تفاعلات جديدة باستخدام أشعة الشمس في وجود الأصباغ العضوية المحفِزة ضوئيا عبر مفاعل صغير. لقد قمنا بنجاح بتصنيع العديد من المركبات العضوية في مفاعل الشعرية كما نجحنا في عملية تحلل الفينول في المياه، وكذلك قمنا بتحديد الظروف الأمثل للتفاعل. التحفيز الضوئي باستخدام الأصباغ العضوية في تفاعلات الزمرة الوظيفية للأمينات الثالثية عند الموقع (أ)، الأوكسي امينيشن لمركبات ١ ، ٣ – ثنائي الكاربونيل عند الموقع (أ)، وفي عملية تحلل الفينول في المياه يمكن ان يكون نموذج لتطوير طرق صديقة للبيئة تساعد في عمليات التخليق الضوئي و التحلل مع الأخذ بعين الاعتبار جميع الخطوات المتبعة. الإستفادة من الإشعة الشمسية غير المركزة في المملكة العربية السعودية تجلى في جامعة الملك فهد للبترول والمعادن. في ما يقرب من جميع التجارب، الإشعاع الشمسي على مفاعل الشعرية أعطى عائدات أعلى من ٦٤ ٪ وإزالة للفينول في المياه الملوثة بنسبة وصلت حتى ٨٦٪.

CHAPTER 1

INTRODUCTION

1.1 Background

Solar based energy is a viable choice to provide energy although it is seasons specific and highly sporadic. Many research works have been conducted to establish better and efficient ways to harvest solar energy to meet the increasing energy needs of the world. First and for most solar energy is clean, renewable, abundant and can easily be trapped. Its environmental friendly nature has given the first priority to be renewable alternative energy resources in the 21st century.

Renewable energy system has been proposed by many researchers to meet the raising energy demand and use of locally available sources. In this technology, renewable energy sources like solar, wind, Micro Hydro Power (MHP), biomass, biogas etc. can be considered for energy generation in many occasions including industrial and domestic application for energy efficiency and energy conservation (Chauhan & Saini, 2014).

Many research works have been conducted to establish better and efficient ways to harvest solar energy to meet the increasing energy needs of the world. Photovoltaic (PV) cells are one of the common known prevalent way to capture solar energy, but unfortunately the efficiency is relatively low and the high cost associated to it hampers its use. Another challenge is limited availability of good quality produced for traditional silicon PV cells.

Solar thermal power system provides a better alternative of higher than 40% and excellent cost-effectiveness.

Systems of harvesting solar thermal power can generally be categorized into two main sets that's concentrating and non-concentrating. Concentrating type collectors usually direct light from large area to a smaller area by the use of mirrored surfaces where the absorber material is located, the intensity is increased by focusing it on one small area while non-concentrating systems without any intermediate directly absorbs photons.

In a concentrating collector, temperatures can reach 300–400 °C and therefore need large concentration in order to reach maximum temperatures, and increase in concentration decreases collector's field of view this renders diffuse light less and less effective. Using only direct sunlight involves many parameters that are inevitable like weather, different wavelengths and reflective surfaces of systems used also degrades over time, especially in the sandy and dusty desert conditions where they are usually operated (Real, Johnston, Lauer, Schicho, & Hotz, 2014).

Kingdom of Saudi Arabia is blessed with high intensity of solar light throughout the year. Sunlight is cheap, non-polluting, plentiful and limitless renewable source of clean energy. Solar energy is thought to be virtually unlimited in the long term, and is a very plentiful resource in Saudi Arabia. It is probable source of renewable energy choice that is being utilized by many countries with even low solar radiation of 3 kWh/m^2, in an effort to decrease their dependence on fossil- fuel based non-renewable energy and reduce environmental effects.

Saudi Arabia is situated in the middle of the world most productive solar regions, which obtains the most powerful kind of sunlight particularly during the summer seasons. The

annual average solar radiation received on the Arabian Peninsula in general is about 2200 kWh/m^2. The geographical area between latitudes 40N and 40S in the world is referred to as Sun Belt, and Saudi Arabia falls between latitudes 31N and 17.5N which is within the range. Saudi Arabia is suitably placed in the world Sun Belt region to take advantage of solar energy. Average solar radiation in Saudi Arabia records between a maximum of 8.004 $KW/m^2/h$ at the city of Bisha and a minimum of 4.479 $KW/m^2/h$ at the city of Tabuk. The high solar radiation value >5 $KW/m^2/h$ are experienced in most parts of the country (Kazmi, 2014).

Utilization of solar energy in different ways in this part of the world is vital. Research, development, and demonstration (RD&D) activities in Saudi Arabia have established that solar energy has a lot of practical uses. Renewable energy is essential factor that deserves intensive research in Saudi Arabia however many national energy specialists in the country have worked on solar energy in the national energy policy.

In the near future energy utilization need to focus on renewable energy technologies like solar energy so that environmental impacts can be decreased (Hepbasli & Alsuhaibani, 2011).

Environmental complications are continuously growing in terms of pollutants, hazards and ecosystem degradation over broader areas. Technological advancement is also associated to dramatic change taking place in the world in many different ways. However, progresses and developments are associated it, no doubt profound environmental difficulties and challenges accompanied with it threaten man and nature. For the last 20 years the

environmental destruction and pollution to the environment have become more obvious. The increasing environmental challenges can be attributed to many factors the number one is human activities that has increased due to growth of world population, consumption, and industrial activities. Effluent gases such as SO_2, NO_x, particulate matters, CO and CO_2 are another notorious environmental pollutants associated with fossil fuels and non-renewable energy (Stambouli, 2011).

As the human population is becoming more mindful of the alarming environmental disturbance caused by human industry, the development of methods to efficiently harness the energy of solar irradiation has emerged as one of the central scientific challenges of the twenty first century (Albini & Fagnoni, 2004a; Protti & Fagnoni, 2009; B. H. D. Roth, 1989). However, the key challenges for solar light based photochemistry are

(i) The lack of photoactive compounds absorbing in the visible region of the sunlight reaching Earth's surface

(ii) Requirement of dense natural sunlight (Hoffmann, 2008a; Mattay & Griesbeck, n.d.; Ramamurthy, 1997). And

(iii) Another obstacle is the requirement for specialised photoreactors to generate high intensity UV light or to concentrate natural sunlight.

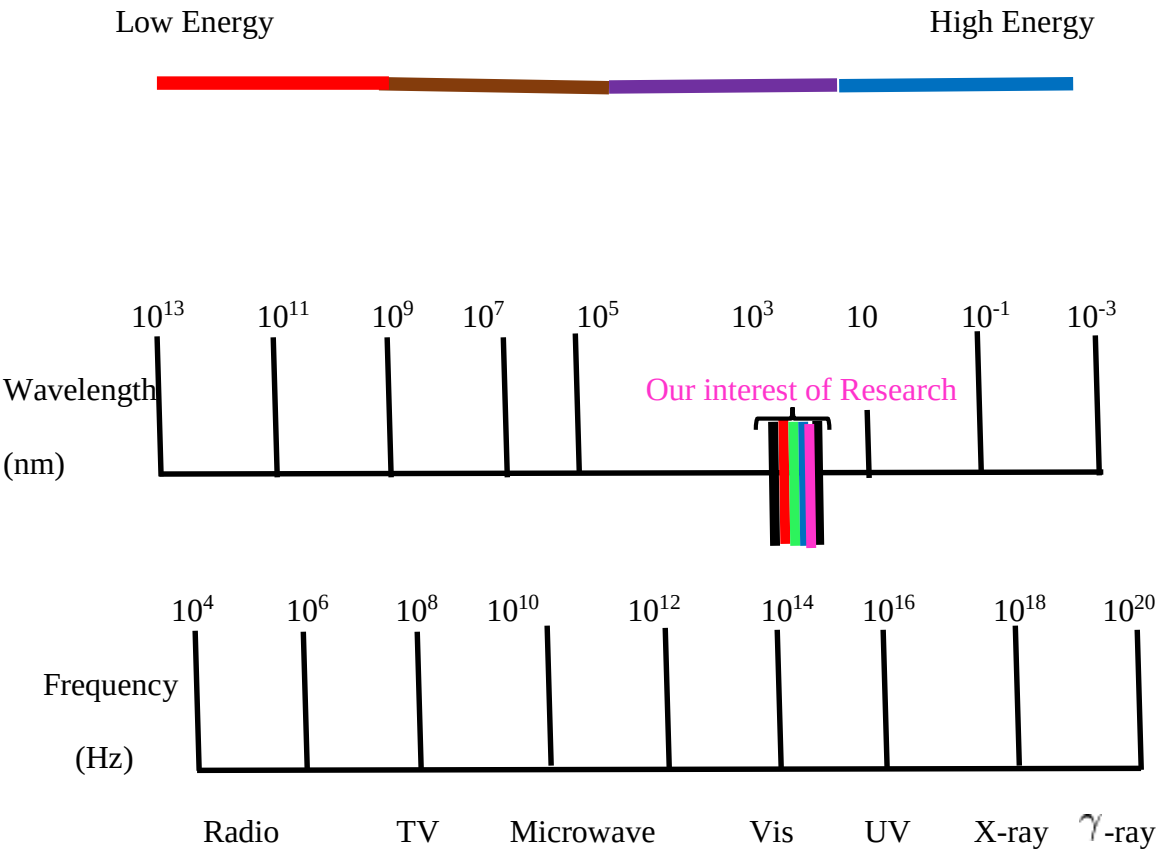
Hence, it is particularly important to develop efficient visible light photo catalysts for synthetic transformations. In this context, for the first time continuous flow micro reactor was developed for synthesizing useful organic compounds and degradation of phenol in water using solar light in the presence of organic dyes as photocatalysts.

In the last 20 years, continuous flow microreactors have appeared as a new tool for both synthetic and process chemists to improve the product yield (Webb & Jamison, 2010; Wegner, Ceylan, & Kirschning, 2011; Wiles & Watts, 2012). Microreactors are series of channels that have sizes which range between 10–500 μm) fixed into a solid substrate. According to synthetic chemistry the reactors are mostly made of glass or even metal to make sure material compatibility of the regents and solvents used in the study or the synthesis; although, frequently used device for analytical works as well are polymeric materials (Wiles, Watts, Haswell, & Pombo-Villar, 2005).

Furthermore, microreactors are most of the time referred to as ‘chips’ the capillary and tubular reactors normally used for synthetic reactions are few millimetres in diameter. Increasing the reactor dimension reduces mixing efficiency and that can be evaded by incorporating the system with micromixer at the entry point. In addition, the heat transmission in bigger tubes within the microreactors is also decreased.

These microreactors provide various benefits compared to the old and traditional batch reactors. For example, enhanced heat- and mass-transfer characteristics, safety of operation when using highly exothermic, explosive or toxic reagents, precise control over residence (reaction) time, isolation of sensitive reactions from air and moisture, high surface-to-volume ratio, the possibility of automation and the ease of scale-up or operating several devices in parallel (numbering up). In addition, these micro reactors permit for integration of numerous reaction steps and subsequent separations in one single efficient process, which results in an important time-gain compared to traditional batch processes. As a result of these advantages, the use of continuous flow reactor has pulled a considerable amount of attention from environmental chemists.

Photochemistry is category of chemistry that deals with chemical processes and procedures that are started by the absorption of light energy photons and the process is termed photolysis where infrared, visible, or ultraviolet light are involved. Photochemical reactions can either be primary or secondary.



Source (Self drawn)

Photochemical reactions are used in synthetic chemistry to produce several organic molecules. Furthermore, photochemical process such as photosynthesis in plants, photography, ozone formation and solar cells are also some important natural and artificial applications of light.

The usefulness of photochemistry was discovered in 1800 and in 1817 the German physicist Theodor von Grotthus acknowledged that for essential chemical change to take

place light must be absorbed first. In 1841 the American chemist John William Draper noted that degree of reaction is proportional to the intensity of the light absorbed. These observations led to the first law of photochemistry (the Grotthus-Draper law), which states that the amount of photochemical reaction is proportional to the amount of light absorbed and when this happens, the energy of the atom or molecule rises above its normal level that's when it's called excited state or activated state which can undergo different process such as luminescence, energy transfer, photoionization, photo dissociation, rearrangement and reaction.

Max Planck, who is the founder of the quantum theory, accepted that an atom or a molecule can absorb only fixed amounts (quanta) of light energy. This energy, E, he theorized, is proportional to the frequency, f, of the light. The energy of a single quantum of radiation is given by

$$\mathbf{E = h\, f,}$$

Where h is fixed and a constant. After five years later Einstein proposed the existence of the unusual particles photons which later lead to the second law of photochemistry. (Background, 1817).

Organic dyes are type of dyes that are made from plants, flowers or other organic substances. Dyes are normally used to color different items of clothing. These dyes having been produced from natural occurring materials they do not comprise various synthetic chemicals that are found in the other dyes and this made people looking for greener, safer alternatives to turn to these types of approach.

Organic dyes are often safer because they do not contain the dangerous toxins. Some toxins in prolong exposure especially to children skins the body absorbs the toxins which can later have adverse effects ranging from simple skin irritations to body system paralysis unlike organic dyes which can stay on the body surface without absorption.

Globally the demand for dyes and other organic pigments grew by 3.9% in 2013. Textiles industry will ever stay the largest consumer followed by printing inks, paint and coatings, and plastics. Some of the common dyes are like disperse dyes, reactive dyes, acid dyes, direct dyes, basic dyes, azo pigments, phthalocyanine pigments.

However the World Bank estimates that 17 – 20% of industrial water pollution is contributed by textile industry and identified 72 toxic and dangerous chemicals solely from textile dyes coloration and treatment but the figure is relatively far from the percentage pollution contributed by other inorganic materials or non-dye organic substances.

With ecological and environmental concerns gaining momentum the global world of dye industry is also undergoing product mixing transformation as many dyes are being banned. The push is now moving towards the environment friendly natural dyes, which in conjunction with the rising cost of other highly polluting alternatives, creates an opportunity for economies to re-domesticate a portion of their dye production in an eco-friendly manner. (PloughboyOrganic, 2013)

Therefore since the pioneering work of O'Regan and Grätzel, dye-sensitized solar cell (DSSC) fabricated using organic and organometallic dyes has received enormous attention due to their probable advantages such as low cost, facile chemical modifications to fine-tune the functional properties and more so environmental friendliness.

Most of the organic dyes that are used in organic synthesis they become photoexcited by the presence of visible light and accept a photon from the visible light to form their respective excited states as they a reductants and transfer an electron to the substrate via single electron transfer process.

Therefore, the importance of bond-forming strategy for organic synthesis using visible and sunlight has been demonstrated by MacMillan, Yoon, and Stephenson groups (Teplý, 2011).

Furthermore, several photocatalysts have been employed to degrade different pollutants. The commonly used one is TiO_2 because of its chemical stability. Howsoever, TiO_2 works well only in the UV region and not successful in solar irradiation (Bhunia & Jana, 2014).

With all this re-energized interest in organic revolutions initiated by sunlight and very recently also purely organic dyes, as photoredox catalysts, it is interesting to look for the 20th century roots of this branch of organic synthesis and degradation research that uses cheap and free sunlight energy and environmental friendly organic dyes.

Although, many efforts have been devoted to develop the synthetic and degradation process, there is still a requirement to develop novel and efficient synthetic methods from economic and environmental points of view using sunlight and other locally available materials.

In this work we have demonstrated organic synthesis and degradation of phenol in water using sunlight in the presence of organic dyes as catalysts through capillary flow reactor.

Table 1.1 wavelength of light absorption versus color in organic dyes

Wavelength Absorbed (nm)	Colour Absorbed	Colour Observed
400-435	Violet	Yellow-Green
435-480	Blue	Yellow
480-490	Green-Blue	Orange
490-500	Blue-Green	Red
500-560	Green	Purple
560-580	Yellow-Green	Violet
580-595	Yellow	Blue
595-605	Orange	Green-Blue
605-700	Red	Blue-Green

Source ("General Introduction to the chemistry of dyes," 1977)

1.2 Statement of the Problem

Saudi Arabia has abundant sunlight and potential source to perform photoorganic chemistry as green energy. It's the first time, a capillary flow reactor was developed for the investigation of "green organic synthesis" "Organic Pollutants Degradation" using dye as a catalyst. Use of flow reactor has several advantages such as easily scale up the production in large quantities.

Recently, a number of literatures were reported on the use of metal complex photo redox catalysts that use low power visible light irradiated source (Narayanam & Stephenson, 2011). However, use of metal complexes are toxic and expensive, therefore, the

development of visible light inducted reactions is highly desired and promising particularly under metal-free conditions. Organic dyes, which are more environmentally friendly, cheaper and easier to prepare, present a feasible alternative to inorganic photocatalysts in both organic synthesis and organic pollutants degradation (Liu et al. 2010).

1.3 Significance of the Study

In this work, we have explored number of organic reactions using dye as catalyst (metal-free) in sun light. Reactions were monitored by the high performance liquid chromatography and liquid chromatography mass spectrometry for quantitation. This study has created a new direction in photochemical reactions to investigate reaction product and phenol degradation efficiency in water. This work also will help to achieve some strategic goals under the solar energy technology area, such as establishing a national infrastructure for photosynthesis and pollutants degradation technologies, transferring and localizing high-quality energy technologies, and providing scientific consultation in this specific area of research. This study is in line with energy and environmental friendly synthesis which is strategically important areas to the Kingdom.

1.4 Research Objectives

The main objective of this study is to develop new technological approach to utilize solar energy and organic dyes for synthesizing useful organic compounds and degradation of phenol in water. It is anticipated that the chemical/petrochemical industry will be interested in this work.

Key specific objectives of this research are;

1. To develop and test flow capillary reactor for various photo organic chemistry reactions
2. To develop and optimize the reaction conditions with different organic dyes in sun light radiation.
3. Optimize the reaction conditions to achieve higher yield.
4. To demonstrate degradation of Phenol from contaminated water using graphene oxide and organic dyes under bench-scale condition.

CHAPTER 2

LITERATURE REVIEW

Solar photons is ideal green approach as it is free and leave no residue in the reaction mixture. In many occasions, the solar radiation could effectively be used to substitute the toxic, expensive and environmental damaging chemical reagents to overcome the activation energy in organic synthesis. Solar radiation is the best energy source since it is cheap, clean and available throughout the entire world (Albini & Fagnoni, 2004; H. . Roth, 2000). Photo organic chemistry is a promising approach for solar mediated synthesis since light is absorbed by the photocatalyst and not by organic substrates, inducing reaction also in molecules transparent to solar light.

Using photochemistry is appealing, because excited states of molecules have energy comparable to that of the chemical bonds, and thus allow a deep-seated transformation of the reagent (Hoffmann, 2008; Protti & Fagnoni, 2009). Methods of technically utilizing sunlight in continuous processes can be divided into thermal and photon-linked branches. As shown in (Figure 2.1), the solar photochemistry can be divided into two main areas: solar photochemical synthesis of fine chemicals and solar detoxification processes (Esser, Pohlmann, & Scharf, 2009).

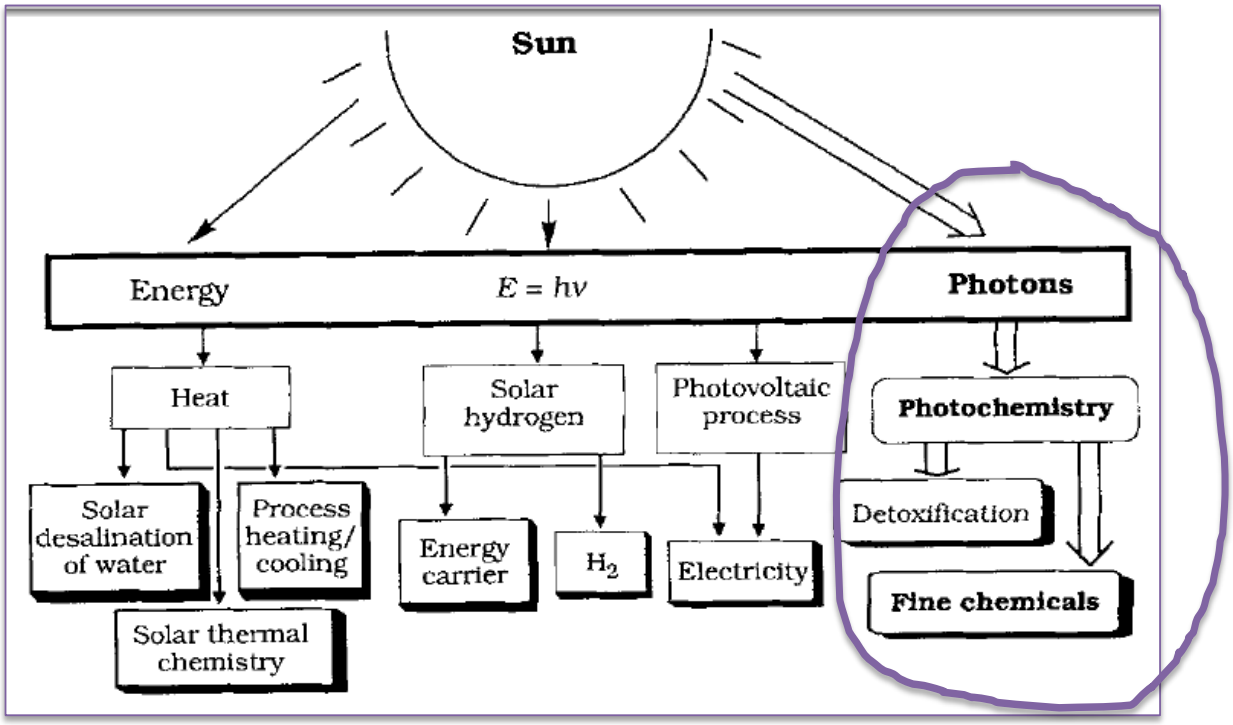


Figure 2.1: Sunlight thermal and photon-linked branches

Sunlight hits the earth's atmosphere with a strength of 1367 Wm^{-2} but its power and spectral distribution is largely altered by it passing through the atmosphere with wind, clouds and other atmospheric players' interaction of the extraterrestrial intensity, 1367 Wm^{-2}. The remaining direct sunlight strength that reaches the earth's surface is approximately 892 Wm^{-2}. If the wavelengths falls below 300 nm, almost no solar photons will be detected on the earth surface. For all photochemical interest regions lie 700 nm because photos of lower energy are not useful in any photochemical reactions. On clear weather the percentage distribution between visible and infrared radiation hardly changes on passage through the atmosphere. In cloudy weather, the infrared radiation is advantaged. (Esser et al., 2009).

The photochemistry can be divided in to two categories: (i) using non-concentrated sunlight and (ii) concentrated sunlight.

In concentrated type, the natural sunlight is the main light source. The utilization of natural light typically has been only limited to traditional ways of transmission, like via the windows but in this modern technological world optical fibres aided sunlight collection and manageable transmission day light system. The day lighting system is an optical-mechanical-electrical technology that converges outside daylight and transmits it into a basement or an intended position like reaction site or room lacking natural light using fibres. The system is normally made of a two-axis tracking system, large-core optical fibres, and lens on top of the tracking system. The usual direct normal solar radiation is converged and concentrated by the lens, focused into large-core optical fibres, and then compliantly transported into the target areas. The technology has been obtaining increasing research interest because of low cost, energy saving, environmental friendly approach and the comfort in using natural light. Therefore, its used in organic synthesis that require high intensity of sunlight (Song, Yang, Zhu, & Jin, 2013).

In non-concentrated sunlight the light is left free and not converged by any lens but directly used. In photoreactions, where starting material electronic excitation is followed by chemical reaction, the light should be a chemical reagent. The light must have wavelength and be able to be absorbed by the material but, for single quantum procedures, it must be available in molar quantities. The quantum yield, is the amount of the product yield to the ratio of radiation absorbed and its usually measured in photons (I Einstein = 1 mole photons), In photocatalytic chain reactions, the quantum yield can be significantly be more than 1. Photochemistry is in an excellent rank to make economically, environmentally and ecologically valuable contributions to the synthesis of highly specialized organic products.

In both concentrated and non-concentrated sunlight approaches, numbers of literatures are available on the batch scale experiments. We have summarized such photochemistry reactions as follows

Synthesis using non-concentrated sunlight (Photocatalytic/photomediated processes, Photodimerization, Cycloadditions, Cyclizations, photoreduction, Synthesis via elimination of a group, Arylation reactions, Isomerizations, Halogenations, Synthesis of endoperoxides, Oxidations/oxygenations, Synthesis via Fischer carbenes. Synthesis via chromoarene derivatives, Synthesis of inorganic materials and solar thermal reactions.

Whereas the *concentrated sunlight* by using solar reactors only few reactions have been demonstrated which includes Photooxidations and photooxygenations, Cycloadditions, Photocatalytic reactions, Photoacylations, E/Z Isomerizations (Hoffmann, 2008; Protti & Fagnoni, 2009).

Photochemical substrate activation often occurs without additional reagents, which diminishes formation of by-products. The photo-oxygenation of furan derivatives has been particularly well studied, and numerous applications to organic synthesis can be found in the literatures. The sun provides a small but continuous photon radiation density. This must be concentrated to obtain high space-time yields in photochemical processes enabling the photoreactor itself to be kept small. Solar photochemical fine chemical synthesis can be used (Albini & Fagnoni, 2004; Esser et al., 2009; Hoffmann, 2008; Protti & Fagnoni, 2009; H. . Roth, 2000). Although the photooxygenations reactions required relatively long illumination times in comparison to the large scale experiments, it must be taken into

account that solar-chemical experiments with non-concentrated sunlight often require several days or weeks to reach high conversion rates.

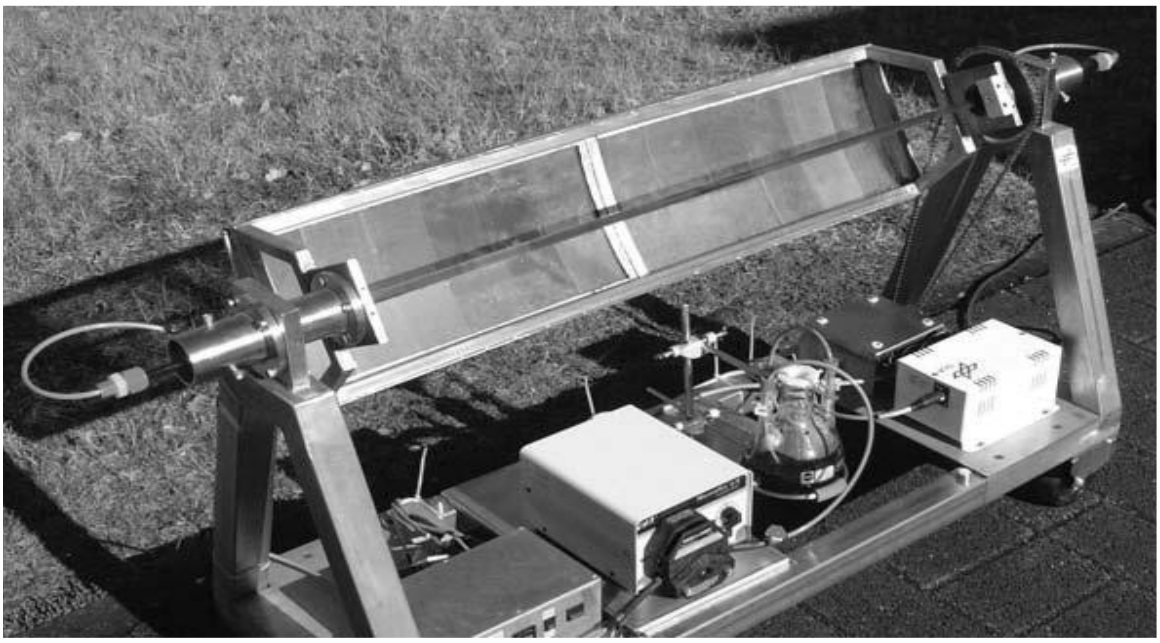


Figure 2.2 shows the concentrated sunlight used for photo organic reactions (H. Roth, 2004)

The trend towards miniaturization has been driven by the need for fast, simple on-line measurements in environmental analysis and medical diagnostics. While initial studies were targeted at analytical applications, it has since been applied to synthetic chemistry in the form of microreactor (Brivio, Verboom, & Reinhoudt, 2006; Fletcher et al., 2002; Haswell & P.watts, 2009; Jakeway, de Mello, & Russell, 2000). The most interesting feature of microreactor is the large surface to volume ratio due to miniaturization (Lo & Ehrfeld, 1999).This gives microreactor excellent mass and heat transfer properties as compared to the conventional reaction vessels, thus allowing better temperature control and eliminating the risk of explosion (Jensen, 2001; Wiles, Watts, Haswell, & Pombo-

villar, 2004; Y.kikutani et al., 2003). Reactions can therefore be carried out under more aggressive conditions (Brivio et al., 2006; Fletcher et al., 2002; Haswell & P.watts, 2009; Jakeway et al., 2000). The large increase of surface area in the microreactor is also beneficial for surface-catalysed reactions. Hence, reactions can be conducted at room temperature. Compared to conventional synthesis, the high degree of temperature control and high mixing efficiency in the microreactor also reduce side-reactions and prevent thermal decomposition, leading to higher yield, selectivity and purity under shorter time frame (Brivio et al., 2006; Fletcher et al., 2002; Haswell & P.watts, 2009; Jakeway et al., 2000). Microreactor also requires fewer reagents and produces less waste. This is cost efficient, safer and beneficial to the environment (Lo & Ehrfeld, 1999).

By connecting multiple microreactors, it is possible to prepare the exact amount of the chemical reagents required at the point of usage (Roberge, Ducry, Bieler, Cretton, & Zimmermann, 2005).

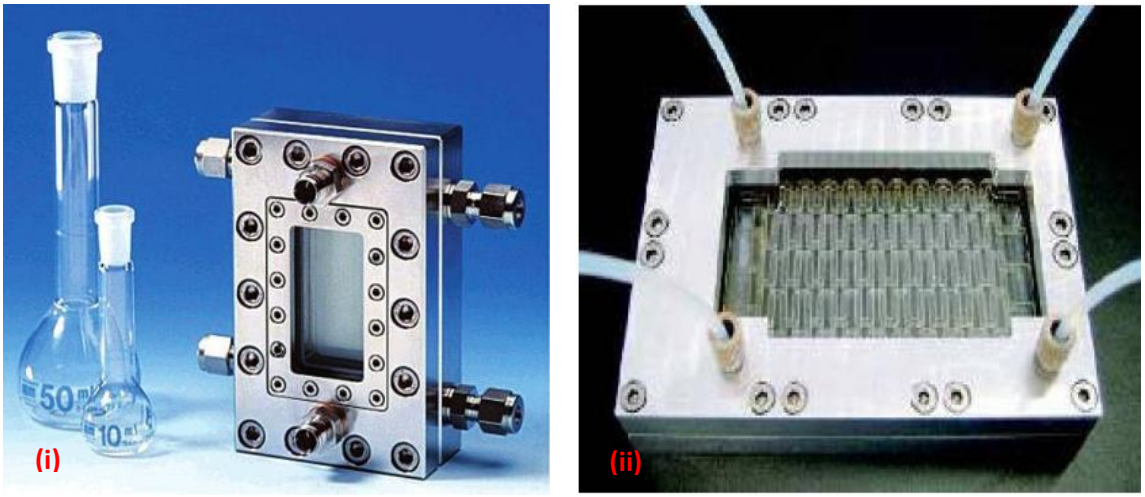


Figure 2.1 and figure 2.4: (i) Dwell device (Mikroglass) and (ii) falling- film microreactor

This minimizes the need to transport and store hazardous or unstable material. It is also possible to scale up production by repeating the same microreactor unit, thus enabling a cost-effective commercial production (Brivio et al., 2006; Fletcher et al., 2002; Haswell & P.watts, 2009; Jakeway et al., 2000).

Recently, micro-structured reactors have become an important topic in industrial chemistry. This technique is particularly useful for the investigation of fast or highly exothermic reactions facilitating isothermic reaction conditions and thus reducing formation of by-products. Using micro structured reactors also increases safety. Several photochemical reactions can be found among the large number of processes already performed in these reactors (Figure 2.3 and 2.4 above shows the Dwell device (Mikroglass) and (ii) falling- film microreactor, as an example.

Batch production is a technology normally applied in manufacturing and it's commonly used in bakeries and other items like sports shoes and pharmaceutical ingredients, purifying water, inks, paints and adhesives where colour run is used. There are a many methods proposed to enhance batch process efficiency but with no much excellence. Some of them are make-span reduction, annual throughput maximization, process measurements, freshwater and wastewater minimization through the exploitation of inter- and intra-process water reuse, batch schedules optimization and/or wastewater treatment, reduction of waste generation, decreasing the necessity of resources, environmental impact assessment, heat recovery and even merging some of the methods to improve efficiency.

In batch processes, the production timeline is critical to obtaining overall productivity and economic effectiveness because the processes are not time independent. A production timetable clearly indicate the series in which products have to be produced, also time taken during the processing operations. Therefore, time line and scheduling has critical duty in heat role in heat integration.

Thermal integration has had no much effects on the batch process in the fact that heat sources and sinks are accessible at less impact on batch processing because the heat sources and sinks tend to be available at different times of the process. In addition heat consumption in batch process is relatively high Pilavachi in his work has developed and emphasized on how to minimize the heat use in the processes (Fernández, Renedo, Pérez, Ortiz, & Mañana, 2012).

Unlike batch reactor technology, which has changed little over the past century, continuous flow reactors form part of a rapidly growing research area which has the opportunity to change the way synthetic chemistry is performed both at a research and industrial level. Compared to stirred tank reactors, flow reactors have significant processing advantages including improved thermal management, mixing control and the application of extreme reaction conditions. Consequently, synthetic processes can be intensified by reducing the volume of solvent employed whilst maintaining control of reaction temperature. With respect to heat and mass transfer, efficient mixing as well as precise continuous flow reactors are generally smaller than batch reactors.

This approach would be particularly advantageous for the fine chemical and pharmaceutical industries, where productions are often in small amount. However, fabrication of the microreactor using photolithographic method requires clean room facilities and expensive instrumentation (Brivio et al., 2006; Fletcher et al., 2002; Haswell & P.watts, 2009; Jakeway et al., 2000). Unlike photolithographic microreactor, the ordinary glass capillary reactor fabricated for Suzuki coupling reactions (Basheer, Jahir Hussain, Lee, & Valiyaveettil, 2004) and the oxidation of glucose (Basheer, Swaminathan, Lee, & Valiyaveettil, 2005), is easily available, affordable and easier to fabricate and handle.

Organic dyes are cheap, more environmentally friendly and easier to modify compared to metal photoredox catalysts. Catalysts are additional substance to increase the rate of a chemical reaction of one or more reactants and it's not consumed by the reaction and can take part in various chemical transformations. The effect of a catalyst may be affected by inhibitors or promoters.

Some of the photoredox catalysts that have been used on this study previously are Dehydrogenative coupling reactions between cyclic tertiary amines such as *N*-aryl-tetrahydroisoquinoline and Nitroalkanes, catalysed by $Ir(ppy)_2(dtbbpy)PF_6$ and similar cyclic tertiary amine with ketones, using a dual catalyst system, $Ru(bpy)_3Cl_2$ and L-proline.

2.1 Tris(bipyridine)ruthenium(II) chloride ($Ru(bpy)_3Cl_2$)

Tris(bipyridine)ruthenium(II) chloride is a combination of different elements with the chemical formula $[Ru(bpy)_3]Cl_2$. Its red crystalline salt made of hexahydrate however the interest property are the only cations of $Ru(bpy)_3]^{2+}$, because it has distinctive optical properties and in some instances chlorides can be substituted with other anions, like PF_6^-.

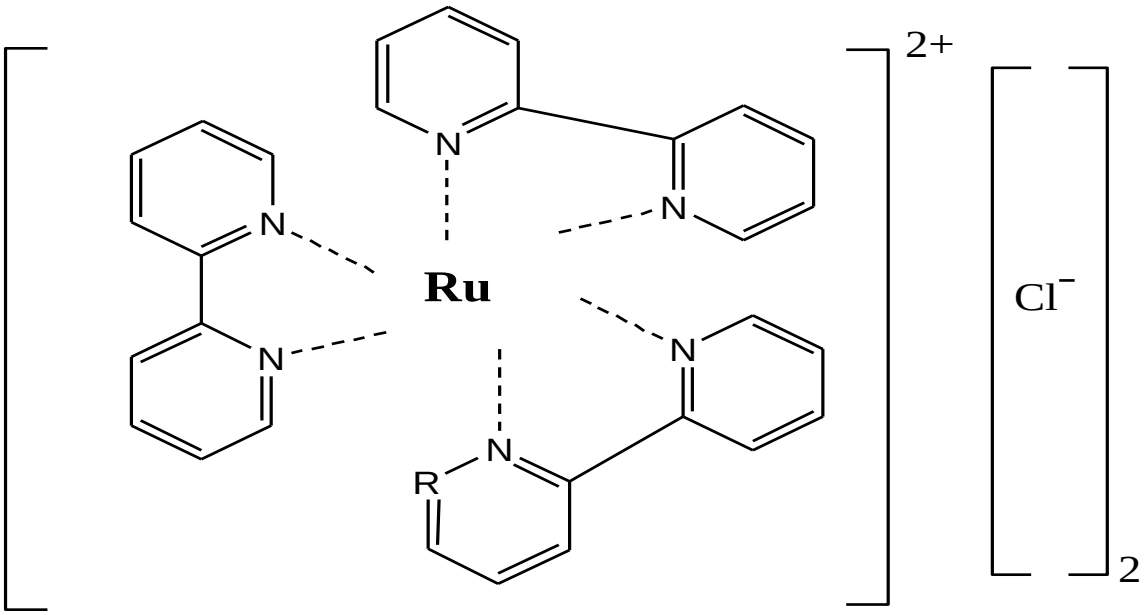


Figure 2 **Figure 2.5: Structure of Tris(bipyridine)ruthenium(II) chloride ($Ru(bpy)_3Cl_2$)**

The preparation of the salt is done by treating an aqueous solution of ruthenium trichloride with 2, 2'-bipyridine. In this process hypophosphorous acid is added as a reducing agent to reduce Ru(III) to Ru(II). $[Ru(bpy)_3]^{2+}$ also absorbs UV light and visible light and in an aqueous state the molecule strongly absorbs at 452 ± 3 nm.

Since 1970s photo redox catalysts that uses addition of $[Ru(bpy)_3]^{2+}$ catalyst and visible light has been utilized in organic synthesis. However, only a few research groups have shown interest dealing with this field until the beginning of the 21st century perhaps because of considering more environmental approaches. From 2008, growth of organic synthesis with bond-forming strategy has obtained a lot of momentum resulted by the series of works done by MacMillan, Yoon, and Stephenson groups. In organic synthesis oxidation and reduction play crucial role and $[Ru(bpy)_3]^{2+}$ catalyst is used to initiate the photoreduction or photooxidation. It is expected that photoredox reactivity of complexes based on metals other than Ru (e.g. Ir, Re, and bimetallic photocatalysts) will be highly explored in the future research works. Additionally, organic photoredox catalysts start to attract researchers because of the cost and environmental friendliness as hinted in the recent report by Zeitler group.

2.2 Rose Bengal

Rose bengal (RB) dye is an anionic water-soluble xanthene and it was discovered 1881, originally synthesized by Rudolf G. The color and spectroscopy of rose bengal like any other xanthene is almost entirely a function of xanthene ring substitution. In the present years, there are many reports of applications and uses of rose bengal such as photocatalytic conversion of oxygen molecules to yield singlet oxygen upon the absorption of green light, therapy of tumors, cancer chemotherapy, inactivating biological species such as vaccinia virus, microsomal glucose-6-phosphatase and trypsin and also topical ophthalmic diagnostic. Rose bengal is a promising in wastewater treatment due to its water solubility,

absorption in the visible region, good quantum yield of singlet oxygen, and its cheap nature (Kakhki, Nejati-Yazdinejad, & Kakeh, 2013).

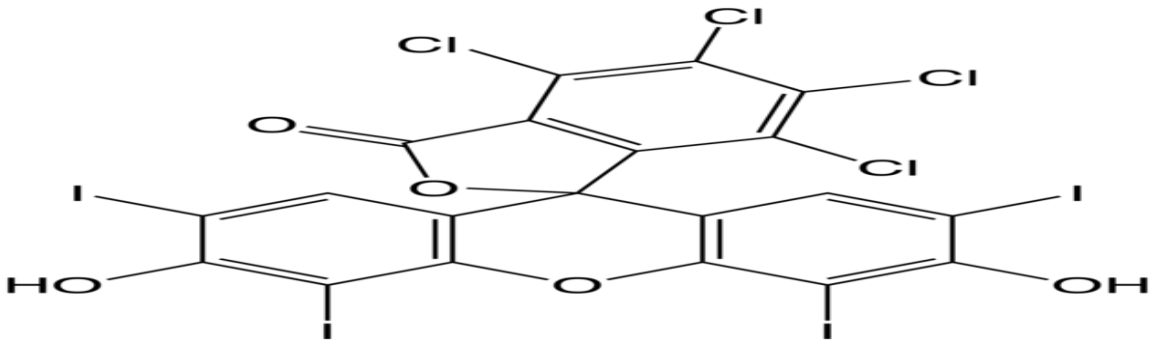


Figure 2.6: Structure of Rose Bengal

The familiar xanthene dyes are fluorescein, eosin, and erythrosin and they differ from rose bengal only in aromatic ring replacement.

All of the spectroscopic properties of rose bengal strictly depend on the ionization state at C-3 and on the type of the solvent. Rose bengal has strong absorbing capacity and plays an active role in many areas of photochemistry. Its spectral properties also allows it to be used as a molecular probe to study chemical environment in a solution or within biological molecules. In addition rose bengal can either be oxidized or reduced in electron-transfer processes depending on the ion (Linden & Necken, 1988).

Rose bengal degradation success in a solution using the heterogeneous photo-fenton process has been studied. It was ascertained that, the heterogeneous photo-fenton process was comparatively more appropriate as compared to its homogeneous colleague. In heterogeneous system the catalyst can be reused and pollution be avoided. Effects of

several parameters like pH, dye concentration, quantity of hydrogen peroxide, light intensity and amount of catalyst on the rate of reaction was critically assessed and also tentative mechanism has been proposed for photo-fenton degradation of rose bengal (Arora, Chanderia, Punjabi, & Sharma, 2010).

Several semiconductors have also been studied as photocatalysts for the removal of different dyes from their solutions. Photocatalytic examination of rose bengal dye removal Zinc sulphide semiconductor was used effectively. Effect of different parameters that affect the rate of reaction like pH, concentration of dye, quantity of semiconductor and light intensity were as well studied in the same study mechanism was also proposed in which hydroxyl radicals are seen as the active oxidizing species (Sharma, Ameta, Malkani, & Ameta, 2013).

2.3 Rhodamine B

Rhodamine B is a dye normally used as a tracer within water to regulate the rate and direction of flow and transport.

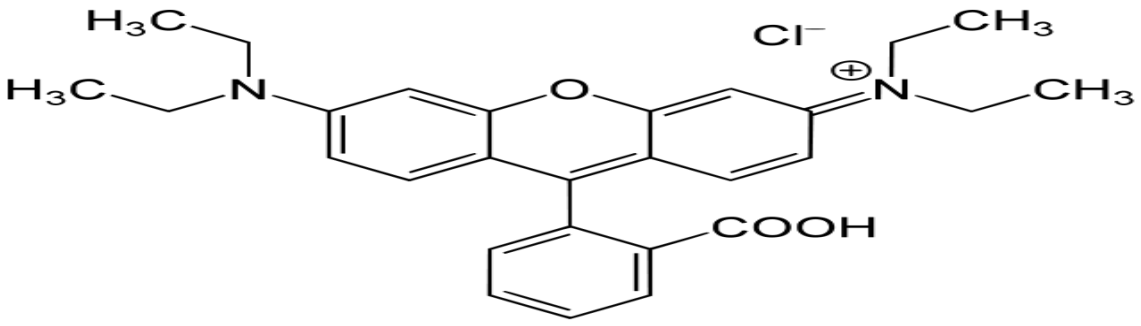


Figure 2.7: Structure of Rhodamine B

Many occasions Rhodamine B has been used as photocatalyst dye. In one instance the visible-light-driven dechlorination of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) was approved with a hydrophobic vitamin B12, heptamethyl cobyrinate perchlorate and Rhodamine B where DDT was effectively dechlorinated to form 1,1-bis(4-chlorophenyl)- 2,2-dichloroethane (DDD) as the mono-dechlorinated product upon visible light irradiation with a tungsten lamp ($\lambda > 440$ nm). (Tahara, Mikuriya, Masuko, Kikuchi, & Hisaeda, 2013).

It is also reported that the hexagonal cone-shaped ZnO nanoparticles in large-scale synthesis by the esterification between zinc acetate and alcohol where ZnO particles show high photocatalytic action for the photocatalytic degradation of Rhodamine B (Ren, Han, Chen, & Tang, 2007).

2.4 Basic Blue 9/ Methylene Blue

Basic blue 9 which is also known as Methylene Blue is a compound containing of dark green crystals or crystalline powder, having a bronze-like luster. It has a deep blue color in both water and alcohol solutions. It is normally used in bacteriologic stain as indicator. In some cases it has been even used to treat cyanide poisoning and to lower levels of Methemoglobin.

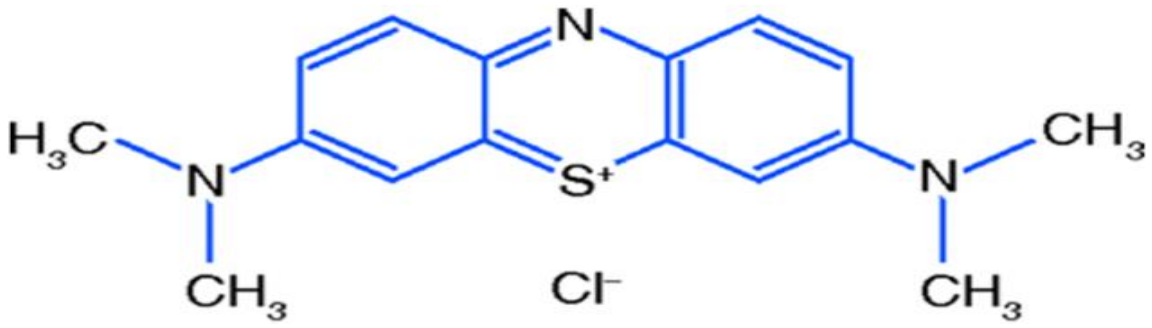


Figure 2.8: Structure of Basic Blue 9/ Methylene Blue

It's studied that synthesis of ZnS/MCM-41 nanocomposite and its photocatalytic action which was assessed using basic blue 9 and methylene blue (MB) under UV light irradiation and it was observed that the degradation effectiveness was reduced in dye concentration above 3.2 ppm for dye. However the best conditions, the degradation efficiency was obtained 0.32 ppm for methylene blue (Pourahmad, 2013).

Also Composite of graphene oxide (GO)/BiOBr was effectively synthesized under visible light using photocatalysts Rhodamine-B (RhB) and methylene blue (MB) and the efficiency was found to be 98% and 95% respectively, when compared to 40% and 50% using pure BiOBr (Vadivel, Vanitha, Muthukrishnaraj, & Balasubramanian, 2014).

2.5 Tetraphenylporphyrin (TPP)

Tetraphenylporphyrin, abbreviated TPP or H_2TPP, is a heterocyclic synthetic compound that look like naturally occurring porphyrins. Porphyrins are dyes that are associated to chlorophyll in green plants and vitamin B12. Porphyrins are difficult to study them due to their low symmetry and the existence of polar substituents. Tetraphenylporphyrin is hydrophobic, symmetrically substituted, and can easily be synthesized. Its dark purple solid compound that dissolves in nonpolar organic solvents like chloroform and benzene.

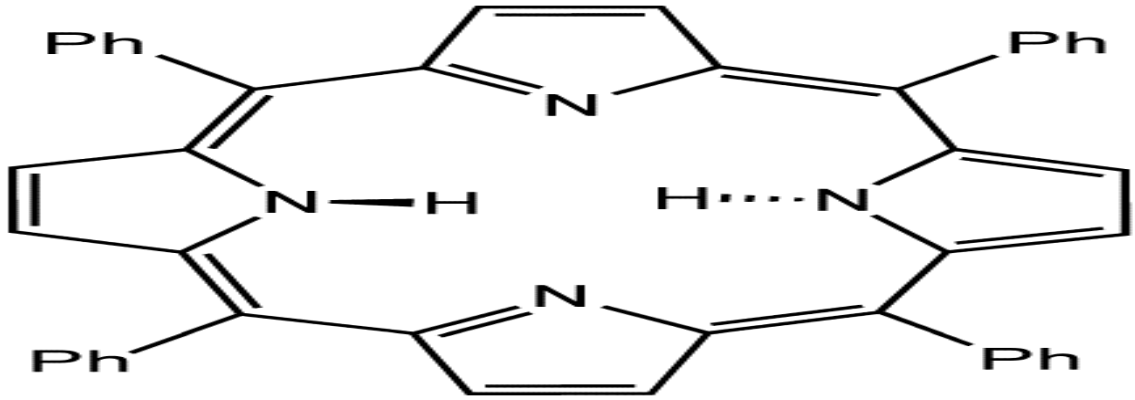


Figure 2.9: Structure of Tetraphenylporphyrin (TPP)

Ishihara and his group studied organic dye enhancement effects on $KTa(Zr)O_3$ and also Ga(Zn)N(O) catalysts which could be much boosted in H_2 and O_2 formation that Cr-Tetraphenylporphyrin (Cr-TPP) and Pt co-catalyst were used. The yield of H_2 and O_2 were 575.0 and 280.4 μmol $gcat^{-1}h^{-1}$ respectively, under Xenon lamp. In their investigation they ascertained that TPP dye modified photocatalyst exhibited the reasonable activity to completely split the water compared to the inorganic photocatalysts.

Also Hagiwara in his group investigated the effects of mixing dye sensitizer for the photocatalytic action of dye-sensitized $Pt/K_{0.95}Ta_{0.92}Zr_{0.08O3}$ and they confirmed that photocatalytic action was far much improved by mixing dye sensitizer on the catalyst, and in their study they used Cr-tetraphenylporphyrin (Cr-TPP) and pentametylene bis[4-(10, 15, 20-triphenylporphine-5-yl)benzoate] dizinc(II) (Zn-TPP dimer) and in addition they proved that the lifetime of the photoexcited electron and hole can be improved by coating with dye sensitizer.

2.6 Fluorescein

Fluorescein is dark orange or rad like powder partially soluble in water and alcohol. It has an absorption maximum at 494 nm and emission maximum of 521 nm (in water) and has isosbestic point that's same absorption for all pH values at 460 nm.

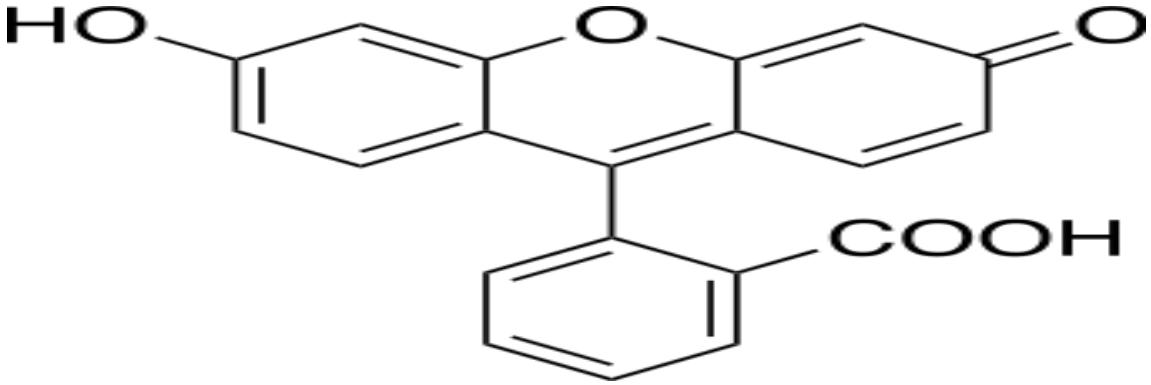


Figure 2.10: Structure of Fluorescein

In a study done by Bi, Zhichu; Tian and Xindi on hydrogen production with Fluorescein and Eosin dyes in aqueous solution where halogen were substituted by dyes photocatalysts , triethanolamine (reducing agent), and K_2PtCl_6 (H generation catalyst) irradiated by a 250 W Xenon lamp. The replacement increased between system crossing that promoted yields of excited triplet states of the dyes and they have also noted the effect which was high in Bromine and Iodine.

2.7 Eosin Y

Eosin Y is one form of eosin that is slightly yellowish tetrabromo derivative of fluorescein. It is normally used to stain material samples such as cytoplasm, collagen, and muscle fibers under the microscope because they are eosinophilic.

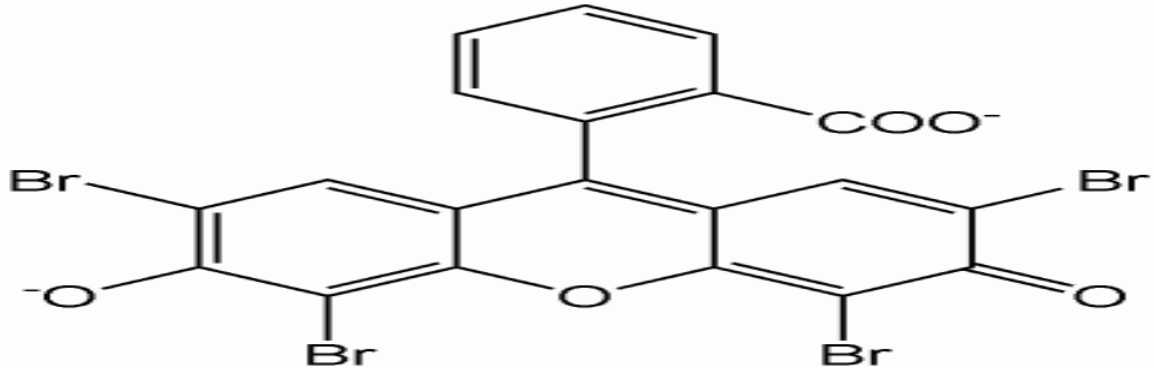


Figure 2.11: Structure of 2-(2,4,5,7-tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl)benzoate (in its deprotonated form)

A visible light of metal-free perfluoroalkylation method catalyzed by dyes for the functionalization of heteroarenes in continuous flow was established and Eosin Y was found to be the most effective photocatalyst dye. Furthermore, quicker reaction was observed in continuous flow with better mixing compared to traditional batch reactor. In the study several pyrroles and indoles were perfluoroalkylated for 30 minutes residence time. (Straathof et al., 2014).

In another study a tertiary photocatalyst composite was designed by impregnation-pyrolysis process where multiwalled carbon nanotubes acted as catalyst and carriers, CuO and Cr_2O_3 acted as a co-catalyst and Eosin Y as a sensitizer. It was discovered that loading CuO and Cr_2O_3 with Eosin Y was essential to obtain the high productivity (X. Li, Zhang, Kang, Li, & Mu, 2014).

2.8 Graphene Oxide

Graphite oxide that is also termed as graphitic oxide or graphitic acid, it composes or contains carbon, oxygen, and hydrogen in different ratios, achieved by oxidation of graphite and turns yellow when fully oxidized.

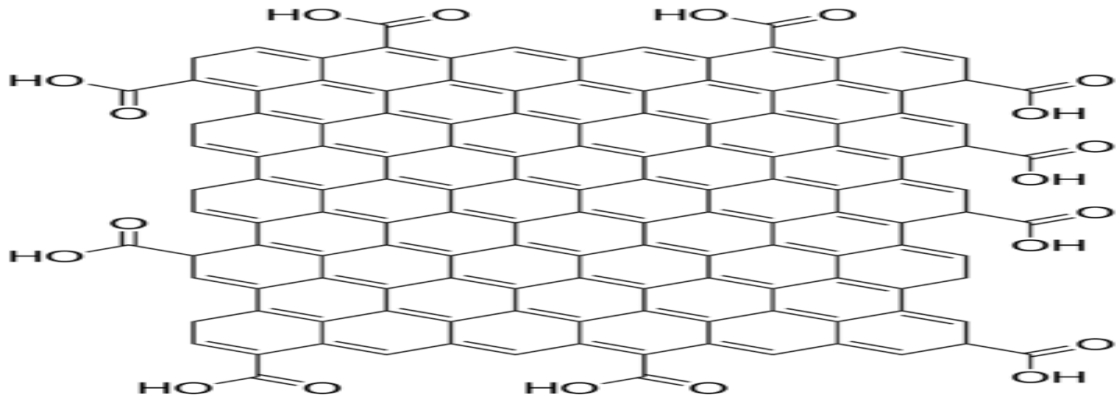


Figure 2.12: Structure of Graphene Oxide

Graphene oxide (GO) photocatalytic features of nanostructures synthesized by modified Hummer's method have been studied under Ultraviolet radiation by calculating decrease rate of resazurin (RZ) into resorufin (RF). The process of the photocatalytic reaction was observed by change in color from blue of resazurin into pink of resorufin and absorption spectra and excellent result was observed showing that graphene oxide has high potential to be used as photocatalyst (Krishnamoorthy, Mohan, & Kim, 2011).

Photocatalytic transformation of carbon dioxide (CO_2) to hydrocarbons like methanol is another landmark approach that uses graphene oxide and reduces risks of energy and environmental issues. The study has also utilized modified Hummer's method. The

photocatalytic reaction has proved six times yield higher than the pure TiO_2 when graphene oxide was used (Hsu et al., 2013).

2.9 TEMPO ((2, 2, 6, 6-Tetramethylpiperidin-1-yl) oxy)

TEMPO which is also called (2,2,6,6-Tetramethylpiperidin-1-yl)oxy, or (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl has formula $(CH_2)_3(CMe_2)2NO$. Its red-orange heterocyclic compound and sublimable solid. As a stable radical prepared by oxidation of 2, 2, 6, 6-tetramethylpiperidine. TEMPO is commonly used in combination with electron spin resonance spectroscopy, as a reagent in organic synthesis, and as a mediator in controlled free radical polymerization and its stability depends on the resonance provided by non-bonding electrons on the nitrogen atom bonded to the oxygen. More stability comes from the steric protection provided by the four methyl groups adjacent to the nitroxyl group. The stability of the radical is further contributed by the weakness of the O-H bond in the hydrogenated derivative TEMPO-H. With an O-H bond dissociation energy of about 70 kcal/mol, this bond is about 30% weaker than a typical O-H bond.

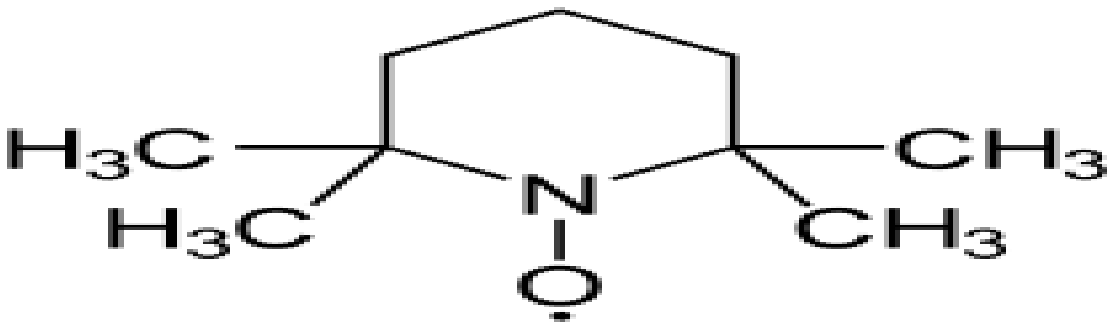
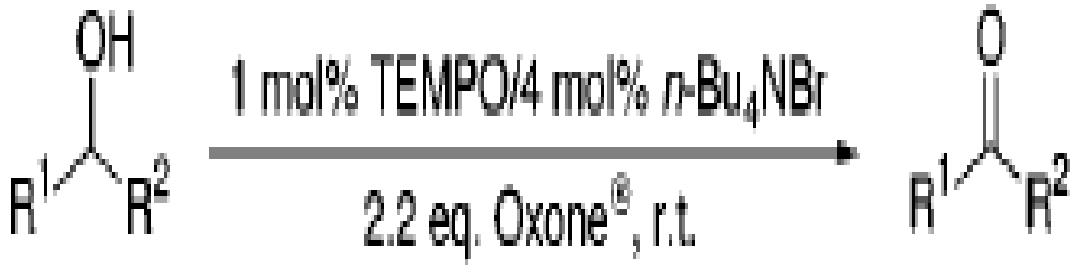
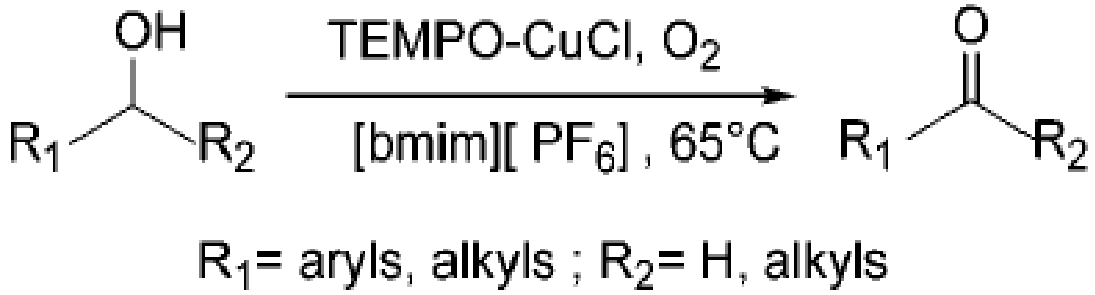


Figure 2.13: Structure of TEMPO

In synthesis of aldehydes and ketones metal-free oxidation system catalyzed by TEMPO/Oxone has been proved. Additionally, in the same study influence of quaternary ammonium salts on the catalysis was studied. The mild conditions of the research procedure were shown to tolerate even sensitive silyl protective groups which can otherwise be sliced in the presence of oxone (Bolm, Magnus, & Hildebrand, 2000).



Further study shows that primary and secondary alcohols catalyzed aerobic oxidation of a simple and mild TEMPO-CuCl to the corresponding aldehydes and ketones in ionic liquid [bmim][PF_6] with no hint of over oxidation to carboxylic acids has been established and the product could be isolated by easy extraction with organic solvent, and the ionic liquid can be recycled or reused (Ansari & Gree, 2002).

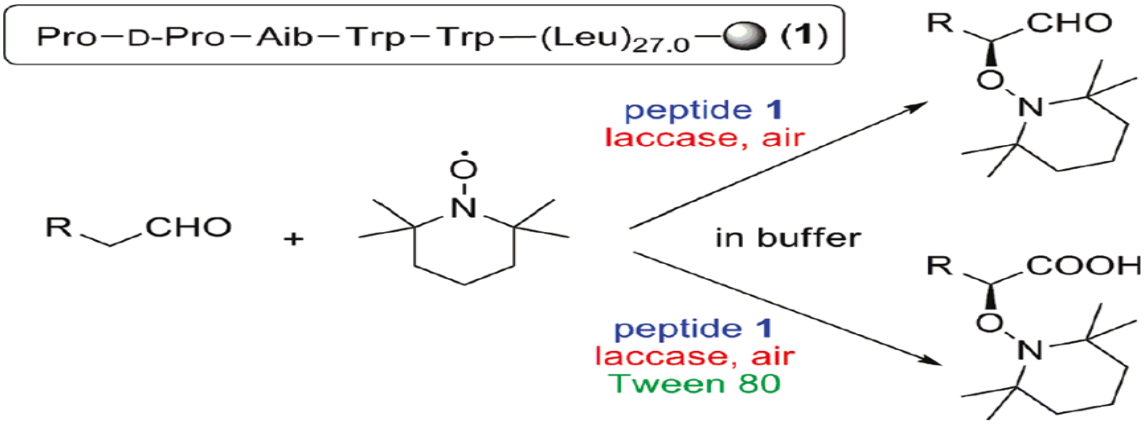


Furthermore, metal free conversion of aryl C-O to C-C bond through a photochemical rearrangement/oxidation cascade reaction is examined where Irradiation of O-acetyl

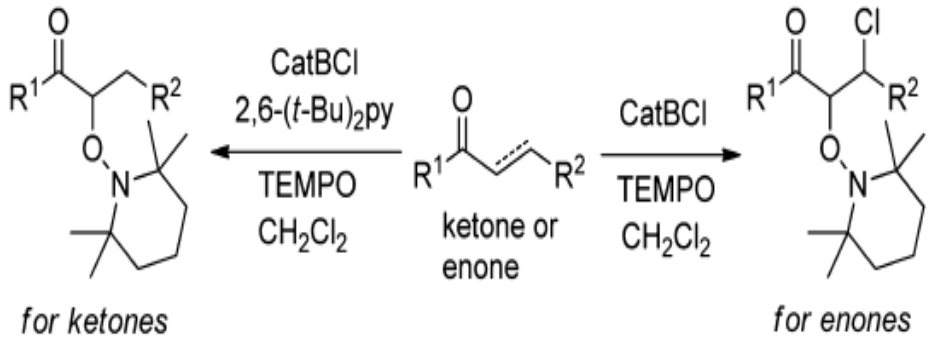
aryloxy benzene derivatives in benzene solution undergoes an exceptional photochemical rearrangement reaction to afford the ketal compounds, which are consecutively oxidized by 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) to produce the diketone compounds (Gou et al., 2012).

2.10 α-Oxyamination

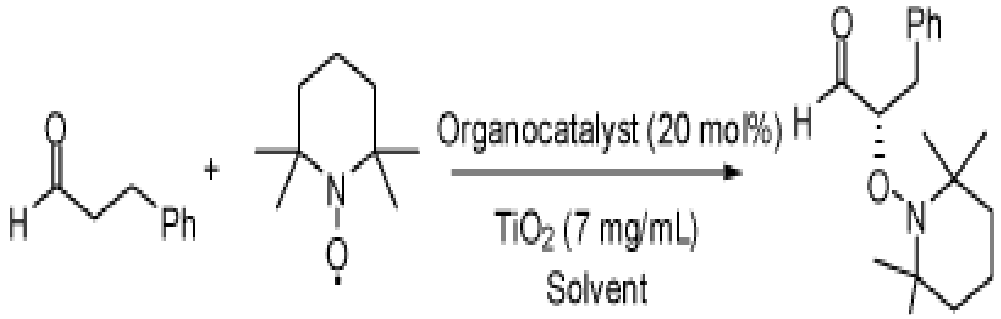
Peptide catalyst and laccase can effectively be used for asymmetric α-oxyamination. The mixture of peptide catalysis and enzymatic air oxidation encouraged the reaction easily in water without using any metal reagent and depending with the reaction condition the oxyaminated compounds could be attained as both aldehyde and carboxylic acid products (Akagawa & Kudo, 2011).



Different oxidation of both cyclic and acyclic ketones have been studied under minor conditions with chlorocatecholborane, a large pyridine base, and TEMPO to the corresponding α-aminoxylated products and remarkable yields ranging 52% to 99% has been reported and enones as substrates, products of a β-chloro-α-aminoxylation are obtained ranging between 70% to 89% (Y. Li, Pouliot, Vogler, Renaud, & Studer, 2012).

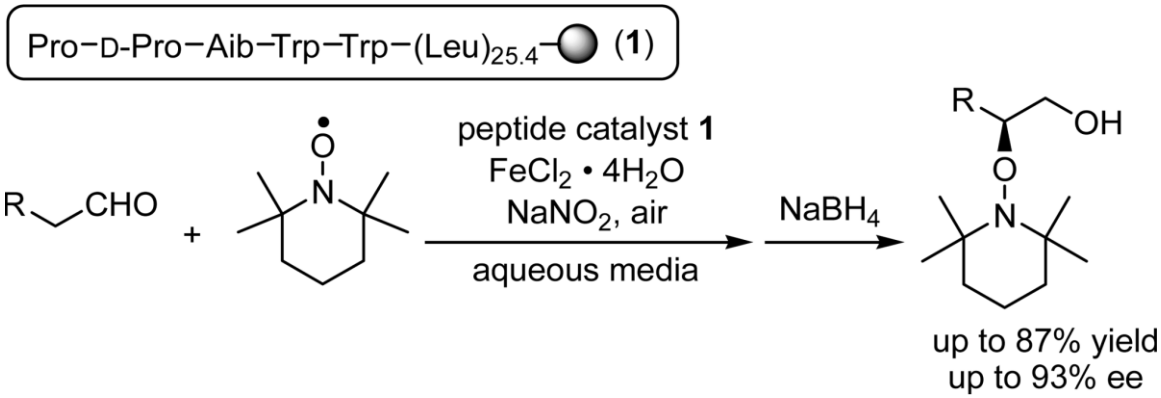


In a green organophotocatalysis study TiO_2-induced enantioselective α-oxyamination of aldehydes has been examined where asymmetric C–O bond formation with various aldehydes under conditions of environmentally friendly photoorganocatalysis has been studied for the first time in chemo- and stereoselective bond formation a heterogeneous TiO_2 photocatalyst is employed as a photooxidant in replacing toxic and expensive chemical oxidants (Ho, Kang, Kim, Park, & Jang, 2011).

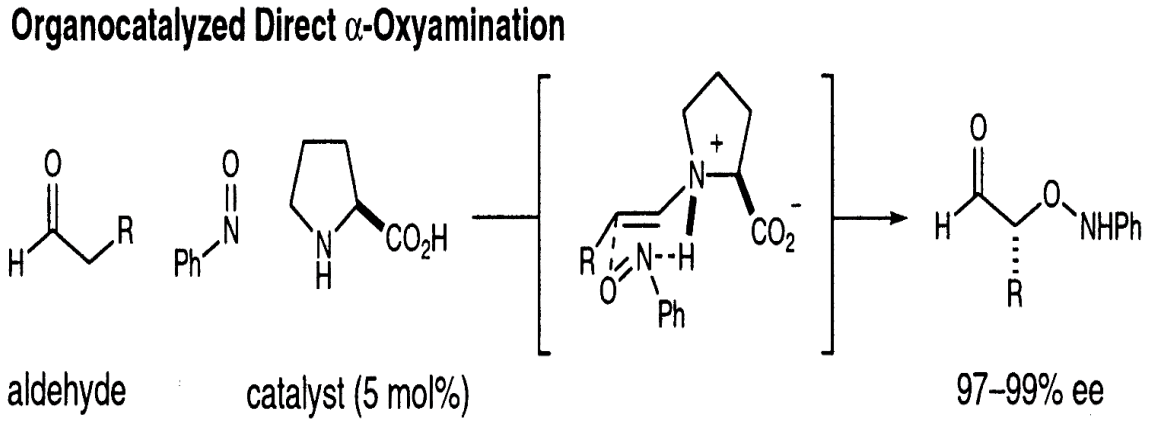


Efficient asymmetric α-Oxyamination of aldehydes by resin-supported peptide catalyst in aqueous study ascertained that the resin-supported peptide catalyst with the end five-residue Pro-D-Pro-Aib-Trp-Trp joined with polyleucine catalyzed the asymmetric α-oxyamination of aldehydes in aqueous media effectively. The reactivity and enantioselectivity have been greatly influenced by the secondary structure and the chirality

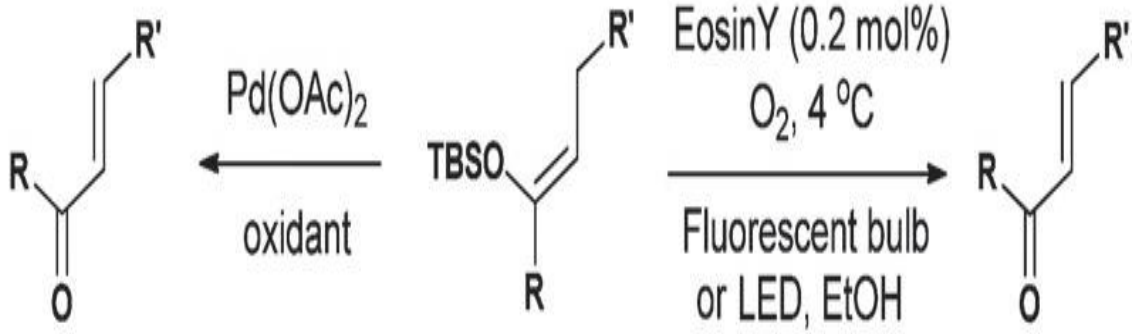
nature of the hydrophobic polyleucine chain according to the study (Akagawa, Fujiwara, Sakamoto, & Kudo, 2010).



In another study the direct and enantioselective organ catalytic α-Oxidation of aldehydes have been considered and successfully the first direct enantioselective catalytic α-oxidation of carbonyls has been achieved. A new organocatalytic approach for enantioselective oxyamination of aldehydes by the use of enamine catalysis to produce α-oxyaldehydes that is essential chiral synthons for natural product and synthesis of medicine. 1-proline is asymmetric catalyst which has been used to facilitate the oxidation with nitrobenzene utilized as the electrophilic oxidant in many different substrates of aldehyde and 2 mol % amount of catalyst were used with successful oxidation taking place with even as low as 0.5 mol % (Brown, Brochu, Sinz, & MacMillan, 2003).

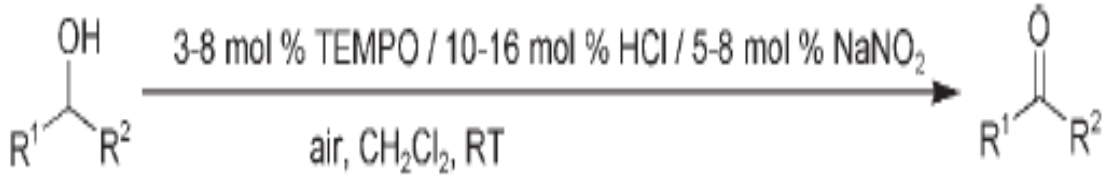


In an aerobic oxidation reaction a cheap organic dye Eosin Y has been used to catalyze α, β-unsaturated ketones and aldehydes synthesis from their corresponding silyl enol ethers in a direct forward and simple process involving a visible-light irradiation. (Zhang, Wang, Liu, Yang, & Huang, 2013).



TEMPO/HCl/$NaNO_2$ combined catalyst of a transition-metal-free approach to efficient aerobic oxidation of alcohols to aldehydes and ketones under mild conditions was successfully proved. Hydrochloric acid (HCl) is inorganic cheap and available acid, with the collaboration of $NaNO_2$/TEMPO was establish to attractively catalyzing the molecular-oxygen-driven oxidation of a wide-range of alcohol substrates to the corresponding

aldehydes and ketones. Particularly, the use of cheap $NaNO_2$ and HCl in mixture with TEMPO for this very selective aerobic oxidation of alcohols in air at ambient temperature and pressure made the reaction operationally and economically appealing. TEMPO, TEMPOH, and TEMPO+ were observed in the redox cycle by means of ESI-MS and mechanism proposed to the development of aerobic alcohol oxidation. (Wang, Liu, Jin, & Liang, 2008).



2.11 Ethyl Benzoylacetate

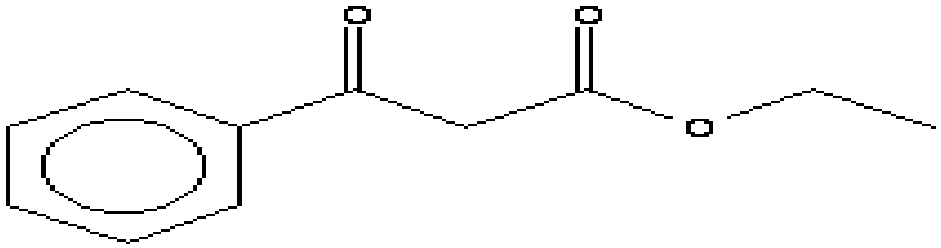


Figure 2.14: Ethyl Benzoylacetate

The synonyms of the compound is Ethyl benzoylacetate, (Benzoylacetic acid ethyl ester); Benzoylacetic acid ethyl ester; ethyl 3-oxo-3-phenylpropanoate Ethyl 3-nitrobenzoylacetate. It's insoluble in water and has refractive index of 1.509.

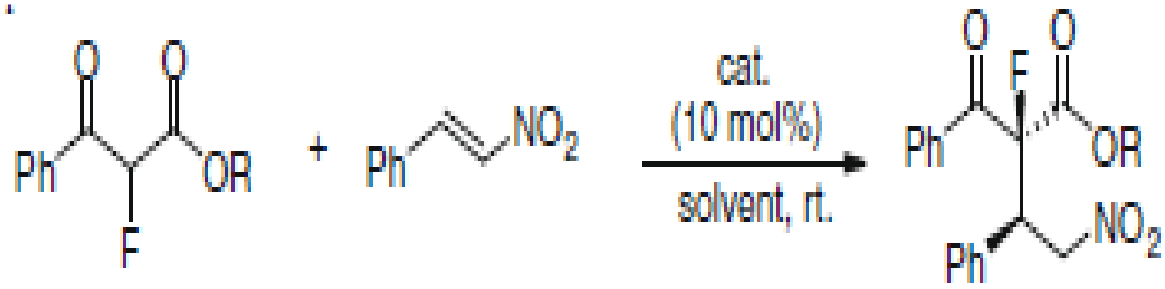
The direct effects of sunlight on the keto-enol proportion of dibenzoylmethane, benzoylacetone and ethyl benzoylacetate in heptane solution was studied. It was shown that the tautomeric equilibrium is highly displaced to the keto form. Essential disparities in the light sensitivity of β-diketones and β-ketoesters regarding the structural features and the nature of irradiation have been ascertained (Markov & Petkov, 1976).

Benzoylation of ethyl benzoylacetate in the presence of various tertiary amines has been studied successfully. In the work condensation of benzoyl chloride with ethyl benzoylacetate has been intensively been examined in four tertiary amines in different solvents. The special product with dimethyl aniline as the solvent was ethyl dibenzoylacetate. In one of the reactions pyridine was studied for two hours at room temperature yielding a 75.8% of ethyl β-benzoxycinnamate and 2.6% ethyl dibenzoylacetate. Using triethylamine as the solvent under the same condition attained 49% of ethyl β-benzoxycinnamate and 29% of ethyl benzoylacetate. Lastly, with quinoline, attained a 17.5% of ethyl benzoylacetate and a 43.5% of $C_{27}H_{23}NO_4$ as product yield respectively and the product $C_{27}H_{23}NO_4$ assumed to be ethyl benzoyl-(l-benzoyl-l,2-dihydro-2-quinolyl)-acetate. The special product with solvent dimethyl aniline was ethyl dibenzoylacetate (Wright & Mcewen, 1952).

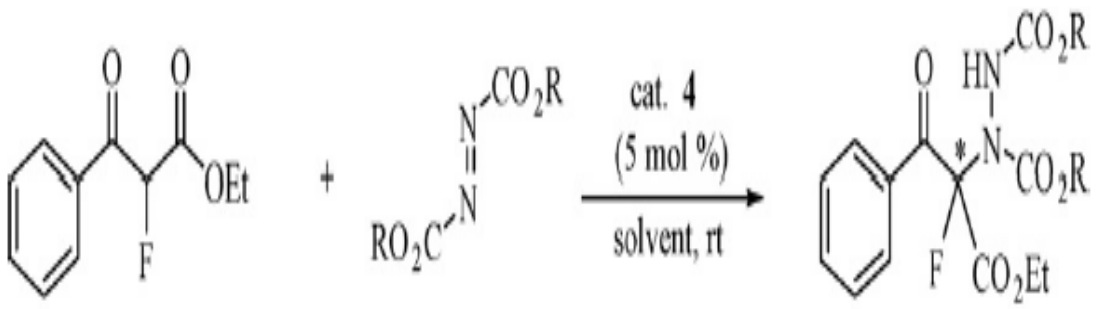
An organic cheap environmentally friendly dye has also been used as photocatalyst to study α-oxyamination reactions between a free radical (TEMPO) and different 1,3-dicarbonyl compounds under visible irradiation light with excellent outcome of 97% yield and when the aromatic benzene ring of ethyl benzoylacetate was replaced with 4-MeOPh, 3-MePh, 3-NO_2Ph, 4-ClPh and 4-FPh a yield of 95%, 84%, 64%, 64% and 67% was recorded respectively (Liu et al., 2010).

2.12 Quaternary Fluoro Compounds.

Addition reaction of α-fluoro-β-ketoesters to nitroalkenes promoted by chiral bifunctional organocatalysts was studied with catalytic enantioselective conjugate under mild reaction conditions and yielded excellent enantioselectivity of over 99% containing a fluorinated quaternary stereogenic center (Oh, Kim, & Kim, 2009).



In another study in catalytic enantioselective electrophilic α-hydrazination encouraged by chiral nickel complexes was explained where in an action of α-fluoro-β-ketoesters with azodicarboxylates as electrophilic amination reagents under mild reaction conditions obtained the corresponding α-amino α-fluoro-β-ketoesters with good yields of 80–96% and enantioselectivity of up to 78% (Mang, Kwon, & Kim, 2009).



Three different continuous flow reactors in a study have been developed and presented in the production and the synthesis of indoles like tetrahydrocarbazole, and cyclopentaindole with good outputs (Wahab, Ellames, Passey, & Watts, 2010).

2.13 2-Fluoro-3-oxo-3-phenyl-propionic acid ethyl ester

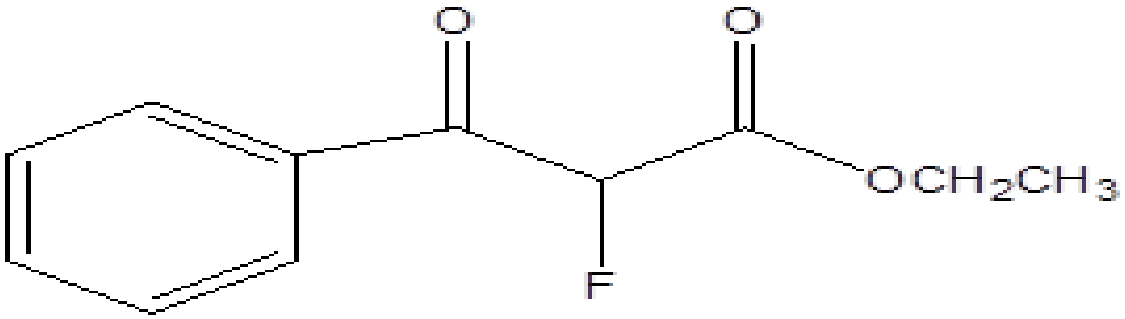


Figure 2.15: 2-Fluoro-3-oxo-3-phenyl-propionic acid ethyl ester

Rose bengal, an organic dye, was used as a visible light photocatalyst to investigate various quaternary fluorinated compounds synthesis using a free radical (TEMPO). This visible light photocatalytic reaction was successfully performed in water and also acetonitrile with

excellent yields and when the benzene was used the yield was 88% and when the benzene ring was substituted with 3-NO_2Ph, 4-ClPh, 4-FPh and 4-MeOPh the yield was 95%, 91%, 90% and 88% respectively (Liu et al., 2010). In this study we have used Ethyl (4-fluorobenzoyl) acetate.

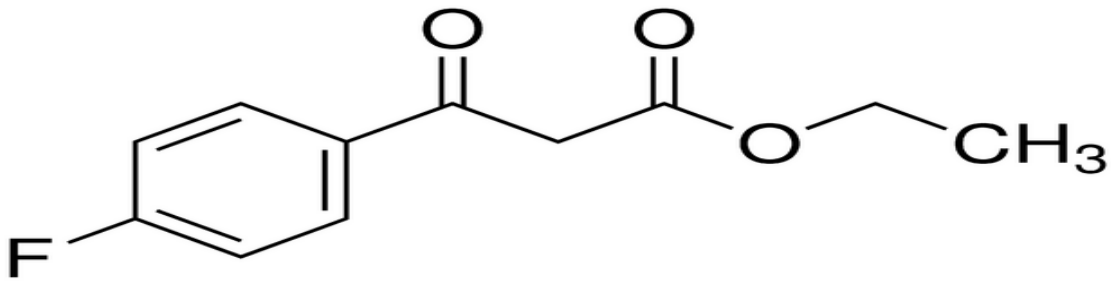


Figure 2.16: Ethyl (4-fluorobenzoyl) acetate

2.14 1 2 3 4-tetrahydroquinoline

Tetrahydroisoquinoline has a chemical formula $C_9H_{11}N$ and is a secondary amine. Like other secondary amines, tetrahydroisoquinoline can be easily be oxidized to the corresponding nitrone using hydrogen peroxide with the catalyst selenium dioxide.

Pharmaceutical drugs such as quaternary ammonium muscle relaxants like tubocurarine usually contain tetrahydroisoquinoline. In this study we have used 2-(4-Bromo-phenyl)-1,2,3,4-tetrahydro-isoquinoline and 2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline as shown in Figure 2.18 and 2.19 respectively.

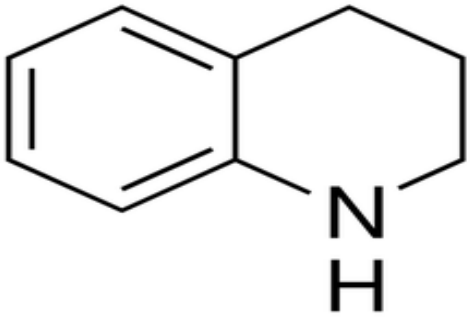


Figure 2.17: 1,2,3,4-Tetrahydro-isoquinoline

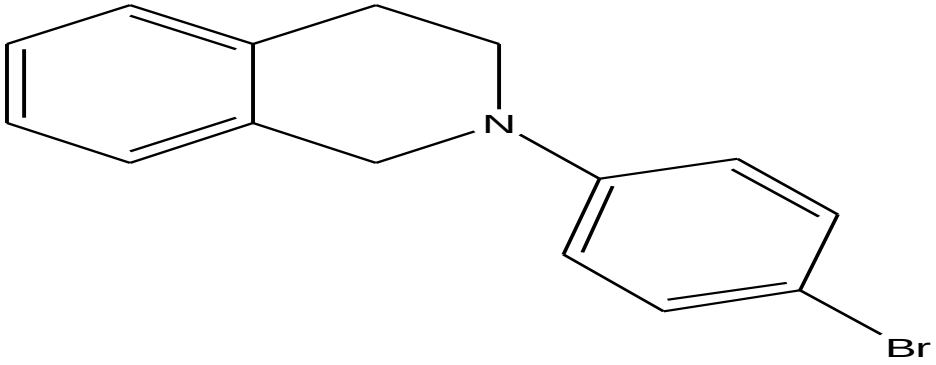


Figure 2.18: 2-(4-Bromo-phenyl)-1,2,3,4-tetrahydro-isoquinoline

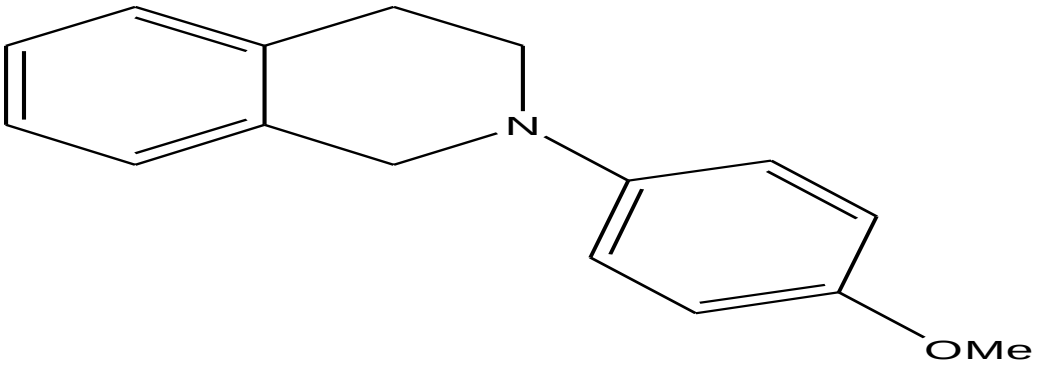


Figure 2.19: 2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline

2.15 Phenol

Phenol which is a priority pollutant was also used in this study for the degradation part. Phenol is a six-carbon aromatic ring that has one hydroxyl (–OH) group, weakly acidic and soluble in water. It has sweet and tarry odour with melting and boiling point of 40.5 ^{0}C and 181.7 ^{0}C respectively (Stewart, Ridge, & Universities, 2008).

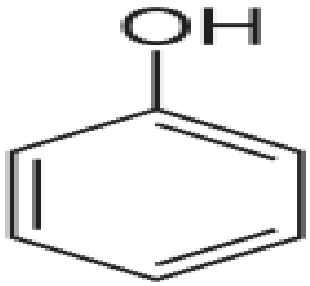


Figure 2.20: Phenol Structure

Phenol is among the eleven phenolic compounds (Figure 2.21) that are regulated because they are priority water pollutants due to their endocrine disruption and toxicity effects. Phenol can end up in the environment through discharge from the industry, use, and disposal of products containing phenol or phenolic derivatives. Phenol in water enters human body through the digestive tract. However, substantial amount can go through skin when come into contact with phenol vapour, liquid phenol or liquids containing phenol.

Phenol in water affects both human health and animals in many ways like cardiovascular disease, serious gastrointestinal damage, respiratory tract and muscle twitching, kidneys problems, liver disease, and lungs complication, muscle tremors, difficulty in walking, and death, blisters and burns on the skin, Vomiting and lethargy in children.

The European community (EC) identified 0.5 µg/L legal tolerance level for phenol in water for human consumption and Japan's Ministry of Health, Labour, and Welfare requires a maximum contaminant level (MCL) of 5 µg/L for phenols in drinking water. The United States Environmental Protection Agency specifies a Maximum Contaminant level of 1 µg/L for phenols and listed it under priority pollutants list. The world health organization recommends lower than 1 µg/L (Shamar, 2013).

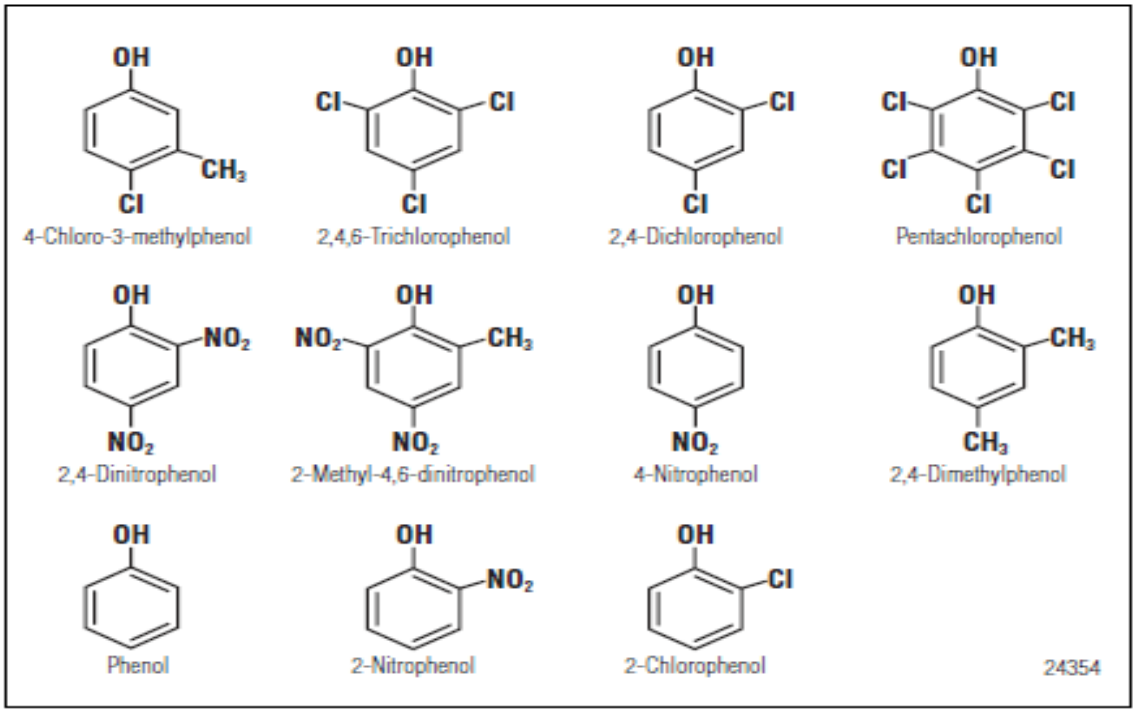


Figure 2.21: Structures of the 11 phenols specified in the U.S. EPA priority pollutants list.

Many research studies have demonstrated both natural and synthetic approach in removal of phenol from water like extraction, adsorption, electrocoagulation, membrane separation techniques, biological method, electron fenton methods were used for phenol removal. Table 2.1 summarizes the removal efficiency of different techniques. (Divate & Hinge, 2014).

Table 2.1 various techniques for phenol removal

Method	Phenol (%) Removal	Limitations	References
Advanced oxidation (UV-TiO_2)	50	Pressure & cost dependency	Nickheslat etal. 2013
Extraction	92.5	Time consuming	V. Archana etal. 2013
Adsorption–flocculation process	90	High initial cost	Yun-Hwei Shen. 2002
Electro coagulation	95 to 95	Film formation on the cathode	Edris Bazrafshan etal. 2012
Biological method (anaerobic)	39 to 80	Takes long time	Azbar etal. 2009
Membrane technique	88	Expensive & membrane lifetime	Gupta 2002
Electro-Fenton (EF-Fere) method	96	40–80 ppm ferrous ion	Jiang etal. 2012
Graphene oxide /Polypyrrole composite	~ 12% to ~ 40%	Low removal	Hu etal. 2015
Reduced graphene oxide/silver Nanoparticle	~ 80%	Pressure dependent	Bhunia & Jana, 2014

Nickel hydroxide catalytic activity in oxidative degradation of phenol in aqueous medium using batch reactor has been studied and explored in respect to effect of time, temperature, partial pressure of oxygen, initial concentration of phenol, catalyst loading and effect of stirring speed on degradation of phenol. It was ascertained that Nickel hydroxide has efficiency in degrading Phenol (Saeed & Ilyas, 2013).

In another study acid-washed zero-valent aluminium (AW-ZVAl) and the technique of using AW-ZVAl/Air/H+ system in the presence of H_2O_2 to remove phenol was fully

examined and it was reported that the method has great potential particularly in organic waste water treatment (Cheng, Fu, Pang, Tang, & Lu, 2015).

Peroxi-electrocoagulation method using mild steel as anode and graphite as cathode has also been investigated to remove phenols from water where the result has shown maximum achievement of 92% removal (Vasudevan, 2014).

New research has established that zinc oxide is more efficient than TiO_2 in visible light photocatalytic degradation of various organic compounds in aqueous solution. Although, many of the studies has been carried out by irradiating zinc oxide suspension with artificial visible light by using microwave irradiated zinc oxide and recent study has shown the efficiency of ZnO to destroy phenol under solar light irradiation (Pardeshi & Patil, 2008).

In another study, photocatalytic degradation of 100 ppm of phenol using titanium dioxide (TiO_2) in aqueous solution was investigated with 94.5% degradation efficiency in 150 minutes of irradiation time. Further it was noted in the same study that the dosage of TiO_2 significantly affected the degradation efficiency of the phenol at 5.2 pH (Alalm, Tawfik, & Chemicals, 2014).

In addition solar photocatalytic degradation of phenol using nano sized ZnO and α-Fe_2O_3 synthesized via precipitation route was studied and it was found that α-Fe_2O_3 exhibits better solar photocatalytic activity than ZnO under identical experimental conditions due to the larger surface area and low band gap of α-Fe_2O_3 (Hamza, J.T, Waziri, & Ajayi, 2013).

Efficient sunlight Photocatalytic degradation of endocrine disruptor bisphenol A (BPA) chemical, in the presence of $Ce_xZn_{1-x}O$ composite nano photocatalyst which has exhibited higher photocatalytic efficiency than pure ZnO in the degradation process under sunlight irradiation was proved to be versatile, economic, environmentally benign and efficient method for BPA removal in the aqueous environment (M, K S, Sivaraj, Kumar R T, & Abdul Salam, 2014).

Clean and green destruction of 2,4-dichlorophenol (2,4-DCP) under natural sunlight using pristine, carbon doped and carbon–iron co-doped electro spun TiO_2 fibers was investigated and the rate of degradation was found to be remarkably high when the intensity of sunlight was >85 kiloLUX and decreased with decrease in solar intensity, however, complete degradation of 2,4-DCP was achieved till very low solar intensity of 20 klx (Raji Rathinavelu & Palanivelu, 2014).

Efficient removal of phenol and aniline from aqueous solution was demonstrated using graphene oxide/polypyrrole (GO/PPy) composites via dielectric barrier discharge (DBD) plasma technique (Hu et al., 2015) and also reduced graphene oxide and silver nanoparticles composite have been ascertained to be efficient in removing phenol and other endocrine disruptors (Bhunia & Jana, 2014)

Highly recalcitrant perfluorooctanoic acid pollutant in water was effectively removed in the presence of sunlight and ferric iron (Fe(III)) which is simple and inexpensive remediation strategy (Liu Danadan et al., 2013).

2.16 Solvent

A solvent is a substance that dissolves a solute resulting in a solution. A solvent is usually a liquid but can also be a solid or even a gas. The concentration of the solute in the solvent varies with temperature. Commonly used organic solvents are tetrachloroethylene, toluene, acetone, methyl acetate, ethyl acetate, hexane, petrol ether, citrus terpenes and ethanol. Solvents are essential in many occasions such as chemical, pharmaceutical, oil and gas industries, including in chemical synthesis and also purification processes.

Table 2.2 Solvents used and their polarity

Polar Solvents		
Solvent	**Chemical Formula**	**Boiling Point**
Dichloromethane (DCM)	CH_2Cl_2	40 °C
Acetonitrile (ACN)	CH_3-C≡N	82 °C
Water	H-O-H	100 °C
Nitromethane	H_3C-NO_2	100 °C

2.17 Acetonitrile

Acetonitrile is colorless liquid is the simplest organic nitrile group generally hydrogen cyanide is a simpler nitrile, but the cyanide anion is not classified as organic and it is used as a polar aprotic solvent in organic synthesis and in the purification of butadiene.

Acetonitrile is utilized primarily as a solvent in extractive distillation and crystallization of pharmaceutical and agricultural products and as a catalyst in synthetic chemical reactions.

It was earlier proposed to be tested by National Cancer Institute due to presence in drinking water and its environmental threat because of lack of enough information on the carcinogenicity of Alkyl Cyanide (Services, 1996).

However acetonitrile has shown to be successful solvent in many organic synthesis. The bovine trypsin-catalyzed synthesis of N-acetyl-l-arginine ethyl ester from N-acetyl-l-arginine and ethanol was assessed using many solvents such as dimethyl sulfoxide, dioxane, dimethylformamide, acetonitrile, acetone, tetrahydrofuran, chloroform, toluene, carbon tetrachloride, cyclohexane and n-hexane but the highest yield of up to 87.7% was obtained when acetonitrile was employed for 6 to 24 hours incubation (Simon, Kotorman, Maraczi, & Laszlo, 2000).

The carboxypeptidase A-catalyzed syntheses of dipeptides from l-amino acids (Phenylalanine, Tyrosine, Tryptophan, Leucine and Ile) were also examined in a different water-miscible organic solvents like acetone, acetonitrile, ethanol, methanol and 1, 4-dioxane and the maximum yield of 43% was observed when acetonitrile with l-Phe as substrate was used for a 24-h incubation. (Vértesi & Simon, 1998).

2.18 Water

Water is very good solvent because of its polarity. When polar compounds get into water, it is surrounded by water molecules. The fairly small size of water molecules will allow many water molecules to surround one molecule of solute. The partly negative dipoles of

the water are attracted to positively charged constituents of the solute, and the same for the positive dipoles. Therefore polar materials like salts and alcohols are soluble in water unlike non-polar like fats and oils

Although irrefutably indispensable, organic synthesis has unfortunately been troubled with its toxicity effects. The use of an organic solvent in many synthesis reactions has drawn more concern. Fortunately, in the recent last year's water is being thought of the best alternative with excellent and surprising yields. In a study by Moulay water was proved to be reliable new synthetic medium and chemist can confidently present his chemistry synthesis work to the public without any doubt (Moulay, 2009).

In a study high yield was observed in donor acceptor butadiene dyes produced by coupling of different 1,1-diaryl-2-propyn-1-ols with indan-1,3-dione. The reactions, which comprised the initial Meyer–Schuster rearrangement of the aromatic alkynols and following condensation of the resulting enals with the β-dicarbonyl compound, continued very well in water, under micro-wave radiation, in the presence of Lewis acid $InCl_3$ (Francos, Borge, Díez, García-Garrido, & Cadierno, 2014)

In another recent research work successful novel method was established for direct *ortho*-acylation of anilides with benzylic alcohols through sp^2 C–H bond activation and it was found that under 40 °C temperature in water with the presence of a catalytic amount of TFA, with TBHP is highly potential to be used in the synthesis of other organic compounds. Further studies and applications of this environmentally friendly direct acylation strategy is also investigated (Luo, Yang, Li, Xiang, & Zhou, 2015).

Therefore in this study we have used sunlight for both organic synthesis and degradation of phenol in water catalysed by organic dyes through a capillary flow reactor.

It's the first time continuous flow reactor is used to perform various organic photochemical reactions and degradation of phenol in water (illustrated in the methodology) we have carried out two organic synthesis reactions (α-Functionalization of tertiary amines and α-oxyamination of 1,3-dicarbonyl compounds) and the degradation of phenol in water. The reaction conditions for both approaches was optimized to achieve higher reaction yield

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Solvents, Chemicals and reagents

Rose Bengal ≥90%, Free radical TEMPO 98% and Dichloromethane ≥99.8% were purchased from Sigma Aldrich. Ethylbenzoylacetate 95% was bought from AK Scientific Inc., Acetonitrile UHPLC Super grade 99.9% was purchased from Panreac AppliChem Company, Phenol ≥96%, Fluorescein dye, Nitromethane ≥95% from Fluka, Eosin Y 88% dye content from Fisher certified biological stains, 2-(4-Bromo-phenyl)-1,2,3,4-tetrahydro-isoquinoline and 2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline from Endotherm life science molecules and graphene oxide was synthesized using hammers method. All the solutions were prepared with deionized water (Siemens Ultra-clear, Saudi Arabia).

3.2 Graphene Oxide Synthesis by Hummers Method

Graphite powder was used to synthesize the Graphene oxide (GO) following modified Hummers method. 2 g of graphite powder and 1 g of sodium nitrate were weighed accurately mixed together then 46 ml of conc. sulphuric acid was added under constant stirring. After 1 h, 6 g of $KMnO_4$ was added slowly to the stirring solution in an ice bar to reduce the temperature less than 20°C to prevent overheating and explosion. The mixture

was further continuously stirred at around 35 °C for many hours and the resulting solution was diluted by adding 280 ml of water under vigorous stirring. In addition the suspension was treated with 30% H_2O_2 solution (10 ml) to ensure the completion of reaction with $KMnO_4$. The resulting mixture was washed thoroughly with HCl and H_2O respectively, followed by filtration and drying for 24 hours in an oven at 60℃, crushed to powder graphene oxide was obtained (Journal, Energy, & Issn, 2014).

3.3 Materials

All the glassware used for this experiments were properly cleaned with deionised water from Siemens Ultra-Clear water purification and finally rinsed with the solvent of interest then oven-dried at least 1hr before use.

3.4 Experimental Setup

Organic dyes are cheap, more environmental friendly and easier to modify compared to metal photoredox catalysts. In fact, several industrial pilot studies had been conducted with organic dyes as photocatalyst (Oelgemller et al. 2005). We have developed new reactions using organic dyes as photocatalyst in the sunlight *via* flow microreactor and number of reactions have been investigated in both synthesis of organic compounds and degradation of phenol in water.

The experimental setup consists of a quartz flow reactor, a magnetic stirrer, a 125ml flask or 50ml measuring cylinder, a mirror for reflection, reactor capillary tubes and a pump.

The schematic diagram of the designed setup for the flow reactor experiments is shown in (Figure 3.2). The photograph of the set-up is also given in (Figure 3.1). The reactor had an inside diameter of 0.4 mm and a length of 1.5 metres and was made up of quartz. The mirror placed below the quartz reactor was purposely to maximize the sunlight intensity through reflection and the pump was to allow continuous flow of the solution. The magnetic stirrer used in the experiments was designed to achieve a homogeneous mixture.

Figure 3.1: Continuous flow photoreactors and the experimental setup used for the study.

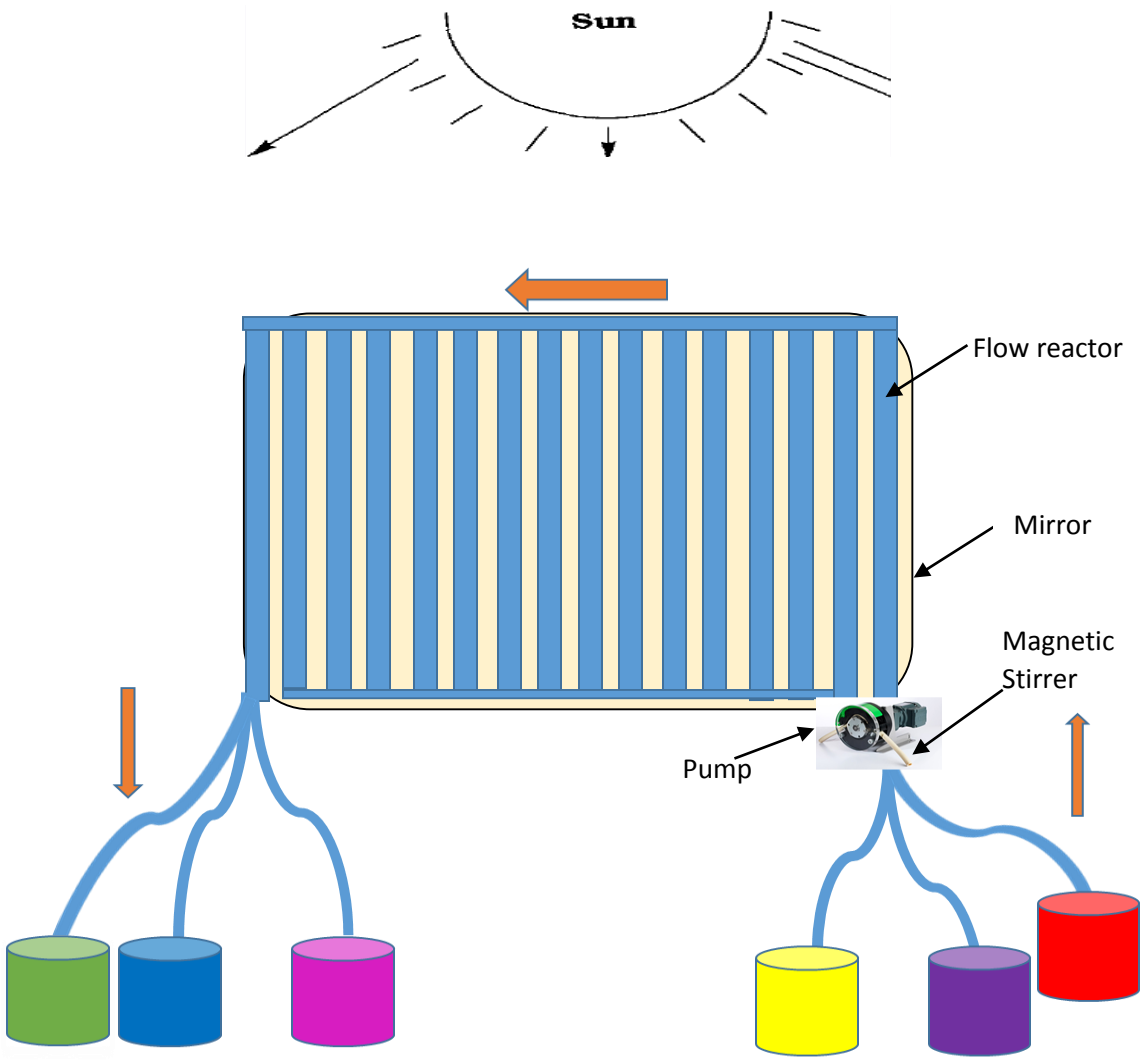


Figure 3.2: Schematic sketch of the Continuous Flow Reactor

Reactions Performed

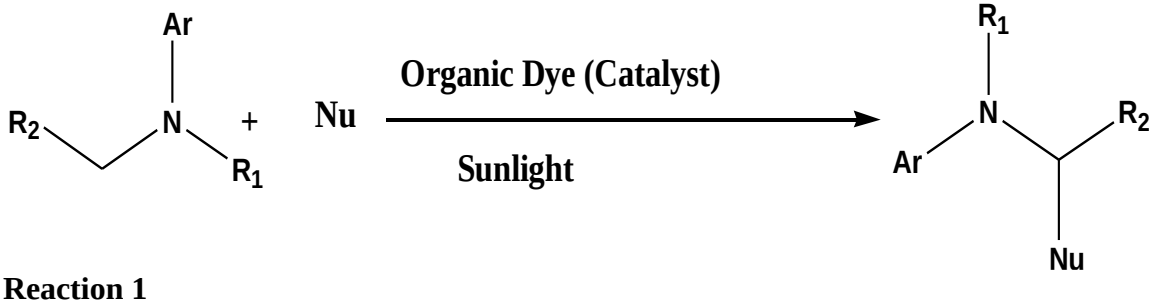
Reaction-1: α-Functionalization of tertiary amines reaction

α-Functionalization of tertiary amines is an important research area as it provides various functionalized amines which are particularly useful in pharmaceutical industry (Pan,

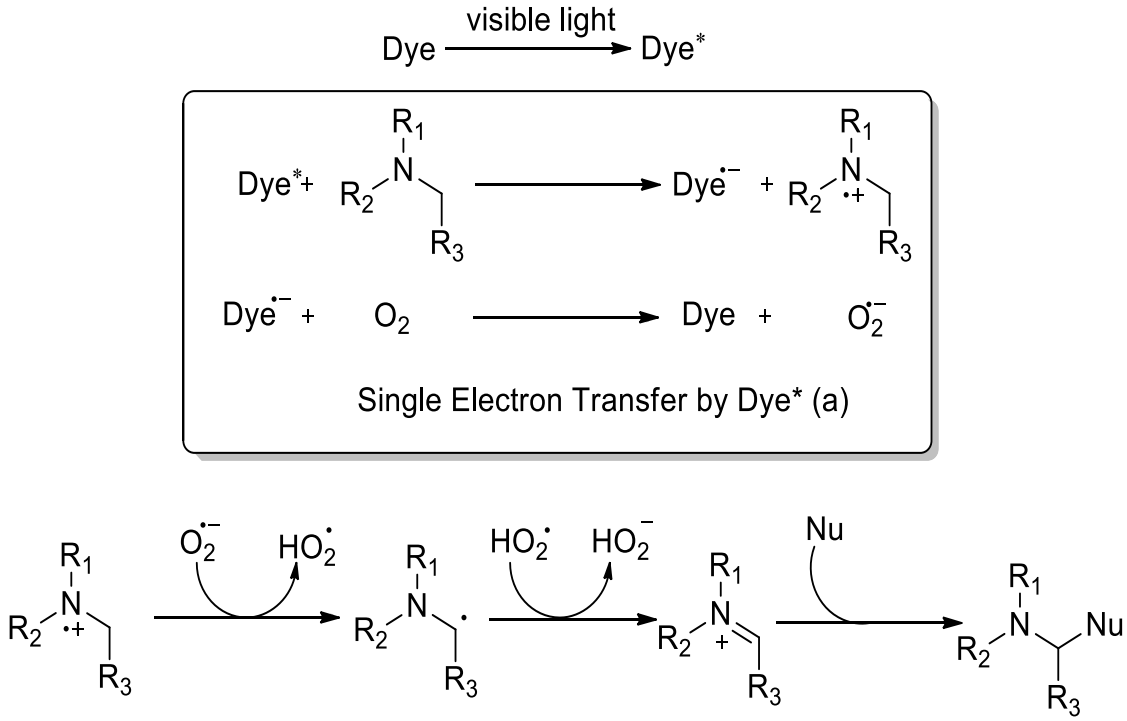
Wang, et al. 2011). However, the α-functionalization of tertiary amines using visible light irradiation is still not very successful as it can only involve some activated tertiary amines. For the inactivated substrates, the reactions are sluggish and some even do not provide products. Although the general formula of this type of reaction is *via* single electron transfer rather than involving singlet oxygen, the detection of the reaction intermediates is still unsuccessful. The chemical yields and reaction efficiency of the slow α-functionalization reactions was improved with the use of the continuous flow reactor.

General Procedure

Dehydrogenative coupling reaction catalysed by organic dyes procedure was followed where the organic dye 250 mg was mixed with 1b which was Nitromethane 50ml and stirred at room temperature for a while and followed by addition of 1045mg of N-aryl-tetrahydroisoquinoline 1a. Then natural air was bubbled for 4 to 8 hours in the reaction mixture using pump before it was injected to the follow reactor under the sunlight irradiation. After certain specified time ranging from 5hour to 48 hours samples were taken and quantified with HPLC and LCMS. The product was confirmed with Nuclear Magnetic Resonance (NMR).



Reaction 1



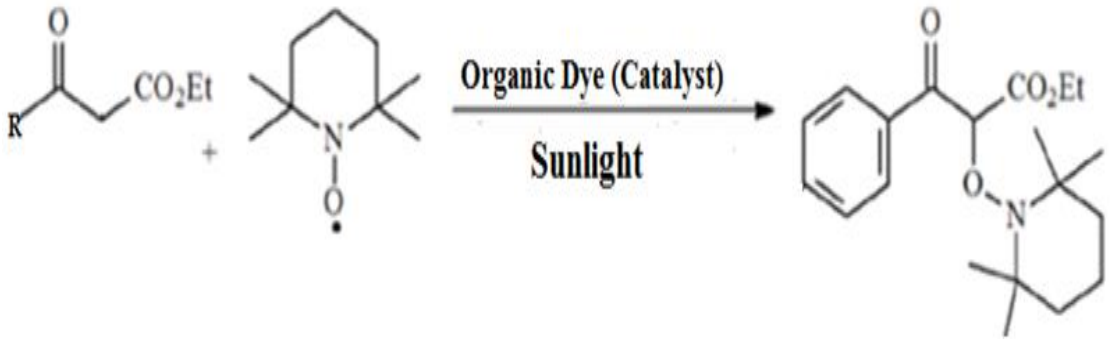
Reaction-2: α-oxyamination of 1, 3-dicarbonyl compounds reactions

α-oxyamination of 1,3-dicarbonyl compounds is a powerful transformation for the synthesis of α-hydroxyl carbonyl compounds (Liu et al. 2010). Although the reaction can be performed under ambient sunlight to give high yield, the reaction time is a bit longer. Taken the advantage of continuous flow reactor, the efficiency of most of the reactions performed were greatly improved. The reaction equation is shown below. With the designed reaction set up, the reaction yield was enhanced.

General Procedure

First (2,2,6,6-Tetramethylpiperidin-1-yl)oxy (780 mg), Rose Bengal (250 mg) and distilled CH_3CN (50 mL) were added in this sequence in a clear 125ml flask. Subsequently stirring at room temperature for a while, ethyl benzoylacetate or ethyl (4-fluorobenzoyl) acetate 2a (900 µL) was added to the mixture. Then, the mixture was irradiated under direct sunlight

using the flow reactor. Afterwards samples were drawn in every specified number of hours from the reaction flask using syringe and injected to the HPLC and LCMS for quantification. The product was confirmed with Nuclear Magnetic Resonance (NMR).



Reaction 2

Reaction-3: Degradation of phenol

Phenol which is one of the priority water pollutant was selected as one of the main human endocrine disruptors to evaluate the catalytic performance of graphene oxide and organic dye.

General Procedure

55 mg of Graphene Oxide: Organic Dye mixture (0.12:0.5, 1:0.12, 0:0.5 and 0.5:0) was dispersed in the 125 mL of phenol polluted water with a concentration of 50mg/L (50ppm) and 200 mg/L (200ppm) and the pH of solutions was adjusted to 3 and 11 by using dilute solution of H_2SO_4 (0.01N) and NaOH (0.01N). The suspension was stirred in dark condition for 2 h to establish adsorption−desorption equilibrium and afterwards the whole set up was then placed in sunlight between 7:00 AM and 5:00 PM through a flow reactor and at different time intervals of 1hour, 2ml of the volume of the solution was taken and

quantified in HPLC. For each of the batch experiments, blank runs were conducted to determine loss to the container/environment, duplicate samples were also collected at the same time and analyzed as a form of quality control to ensure accuracy of experimental results. Also samples were placed in the sun light without the flow reactor to investigate the effects of the flow reactor on the phenol treatment in water. Fourier transform infrared spectroscopy (FTIR) and X-Ray Diffraction (XRD) were used for the characterization of the synthesized graphene oxide.

3.5 Design of Experiment.

In this study Minitab 16 statistical software was used for design analysis and data processing for the phenol degradation. Table 3.1 describes actual and coded levels of the design parameters. Factors were 5, Base Designs were 5, 32, runs were 34 with 1 replicate, blocks none centre points were 2 in total and all of the treatment combinations set in random order to prevent from random error. The result of the factorial design and responding responses were presented on table 3.1.

Table 3.1 Factors and their uncoded levels

Factor	Name	Low	High
A	pH	3	11
B	Phenol Water Conc. (ppm)	50	200
C	Graphene Oxide Dosage	0	1
D	Organic Dye Dosage	0	0.5
E	Time (Hours)	1	10

3.6 Quality control, Data analysis and presentation

Best quality control measures were maintained where the instruments used like HPLC were calibrated with excellent R^2, replicate experiment, duplicate analysis, control and blank samples were run. Data analysis and presentation was done using excel 2010 where the results were presented using graphs and tables.

3.7 Measuring Physical Parameters

During all the experiments the intensity of Sunlight was 0.8-1.2 kWm^2 (Sahin, Aksakal, & Sunar, 1999) and the temperature measured at the site during the experiment times was ambient ranging from 25 ℃ to 36 ℃.

3.8 Characterization

To understand the surface morphology, microstructure and other physical and chemical properties of the Graphene Oxide as an adsorbent, several instrumental studies have been conducted like XRD and FTIR analysis. For the synthesized products both ^{1}HNMR and ^{13}C NMR have been used.

3.8.1 Fourier Transform Infrared Spectroscopy (FTIR)

Characterization of the synthesized graphene oxide was carried out using NICOLET 6700 FT-IR to determine the type of the functional group on the material. The FT-IR, dilution and homogenization was done using potassium bromide (KBr) (spectroscopic grade) from Sigma Aldrich and more grinding was done to completely powder the combination. The disks were pressed in a hydraulic KBr press. The transmission FT-IR spectra were then recorded between 400 and 4000cm-1.

3.8.2 X-Ray Diffraction (XRD)

XRD was employed to identify mineral phases of the synthesized graphene oxide material used for the phenol degradation. Measurements were made using Rigaku MiniFlex II Desktop X-Ray Diffraction instrument. The intensity (CPS) ranging 0-300 and 2-theta (deg) from 0-125 was used for a complete scan.

3.8.3 NMR

Jeol company brand NMR was used for this study with ^{1}HNMR frequency of 10,000htz, 3.2 seconds deposition time and delay time of 40 micro seconds. The ^{13}C NMR parameters were set to frequency 34013.6htz, deposition time of 0.963379b and delay time of 11.8 micro seconds.^{1}H NMR spectra were recorded on 500 MHz in $CDCl_3$ and D_2O and ^{13}CNMR spectra were recorded on 125.65 MHz in $CDCl_3$.

3.9 Instrumental Analysis

3.9.1 High Performance Liquid Chromatography (HPLC)

High Performance Liquid Chromatography (HPLC) Waters 2690 system (Figure 3.3) with UV-Vis Diode array detector was used for the analysis and the stock solution ranging from 10 to 4000 mg/l was used for the calibration of the synthesis part of the study while 10 to 200 mg/l was used for the degradation part to cover for the range of the concentration to be used in the experiments. For all of the concentration analyses, 2.0 mL of the solution was collected in a new glass vial, and 10µL is injected to the column for analysis. Chromatography column was used in the unit (3.9 ×300mm) µ Bonda Pak^{Tm} C18 stationary phase, while the mobile phase was acetonitrile super grade 99.9% UPLC and water with ratio of 60:40 respectively, at a constant flow rate of 1.0 mL/min with wavelength 248nm for α-Oxyamination reactions, for the α-functionalization of the tertiary amine reactions 225nm wavelength and phenol degradation196nm wavelength with mobile phase acetonitrile and water ratio 70:30 respectively. All runs with argon degassing of 20% of the mobile phase and the column conditioned using methanol HPLC grade of 99.9% at a temperature programing of 35℃ ±5. Samples run time was 10 minutes for all the samples.

Figure 3.3: Waters 2690 HPLC

3.9.2 Liquid Chromatography Mass Spectrometry (LCMS)

Liquid Chromatography Mass Spectrometry (LCMS) Shimadzu LCMS-8050 auto sampler PAL HTC-xt connected, CBM-20A communication bus module, Nexera X2/SPD-M30A Diode array detector, DGU-20A5R degassing unit, Nexera X2/ LC-30AD Liquid chromatography, Nexera X2 CTO-30A Column oven was used for the quantification and confirmation of the HPLC results (Figure 3.4). All experiments mobile phase ratio was acetonitrile and water 60:40 respectively with flow rate of 1ml/min and injection volume of 1µ/L. The Mass Spectrometer (MS) temperature for all the runs was 400℃ and Colum oven was maintained at room temperature.

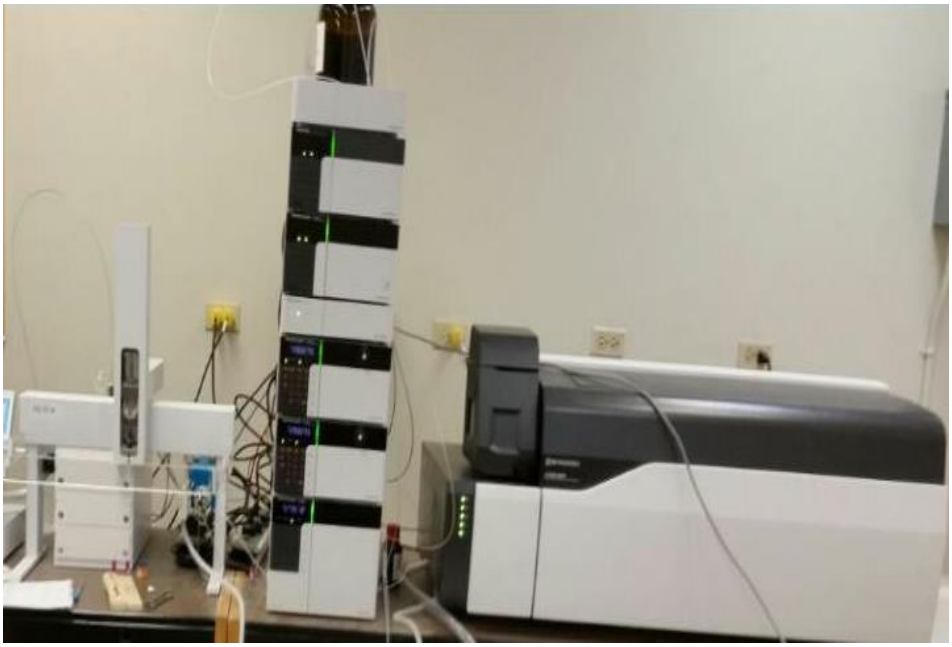


Figure 3.4: Shimadzu LCMS 8050

The formula below was used to calculate the percentage removal (%R) and the percentage yield (%Y)

$$\%\mathbf{R} = \frac{\mathbf{P_O - P_t}}{\mathbf{P_O}} \times \mathbf{100} \quad \text{- - --- - - - - - - - - (1)}$$

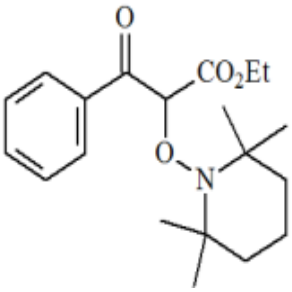
$$\%\mathbf{Y} = \mathbf{Actual\ Yield/Theoretical\ Yield} \times \mathbf{100} \quad \text{-- - - - - - - - - (2)}$$

From the equations above, P_o is the initial concentrations of the phenol while P_t is the final concentrations of phenol.

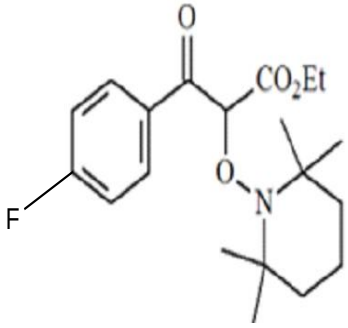
CHAPTER 4

RESULTS AND DISCUSSIONS

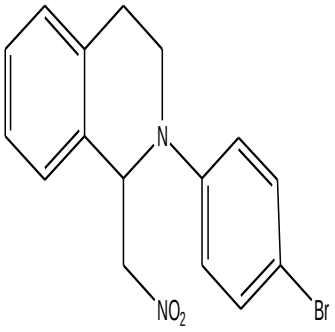
The synthesis of compounds **1c, 2c, 3c, 4c** and degradation of phenol in water is discussed in this study as described in literature. The described procedure by (Liu et al., 2010) reported the α-oxyamination reactions catalyzed by rose bengal, (Pan, Kee, Chen, & Tan, 2011) reported dehydrogenative coupling reactions catalyzed by rose bengal using visible light irradiation and (Bhunia & Jana, 2014) reported reduced graphene oxide-silver nanoparticle composite as visible light photocatalyst for degradation of colorless endocrine disruptors. Both α-oxyamination and dehydrogenative coupling reactions procedures in the previous literatures had reported relatively good results in the synthesis with the use of fluorescent lamp however, with longer duration. When the procedure was scaled up by the use of natural sunlight and the advantage of the flow reactor excellent yields were recorded in a shorter time with pure products and excellent conversion rate.



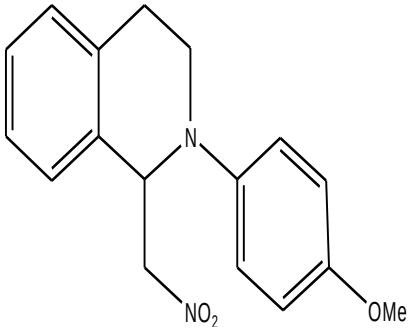
1c



2c



3c



4c

We have first started the study by checking the absorption regions of the light sensitizers and we have noted that the maximum absorbance of rose bengal organic dye is around 550 nm in water (Figure 4.1), eosin Y and fluorescein organic dye had maximum absorbance of 540 nm (Figure 4.3) and 440 nm (Figure 4.4) respectively in methanol solvent. In addition graphene oxide which was used in the degradation of phenol was found to be absorbing around 240nm in water.

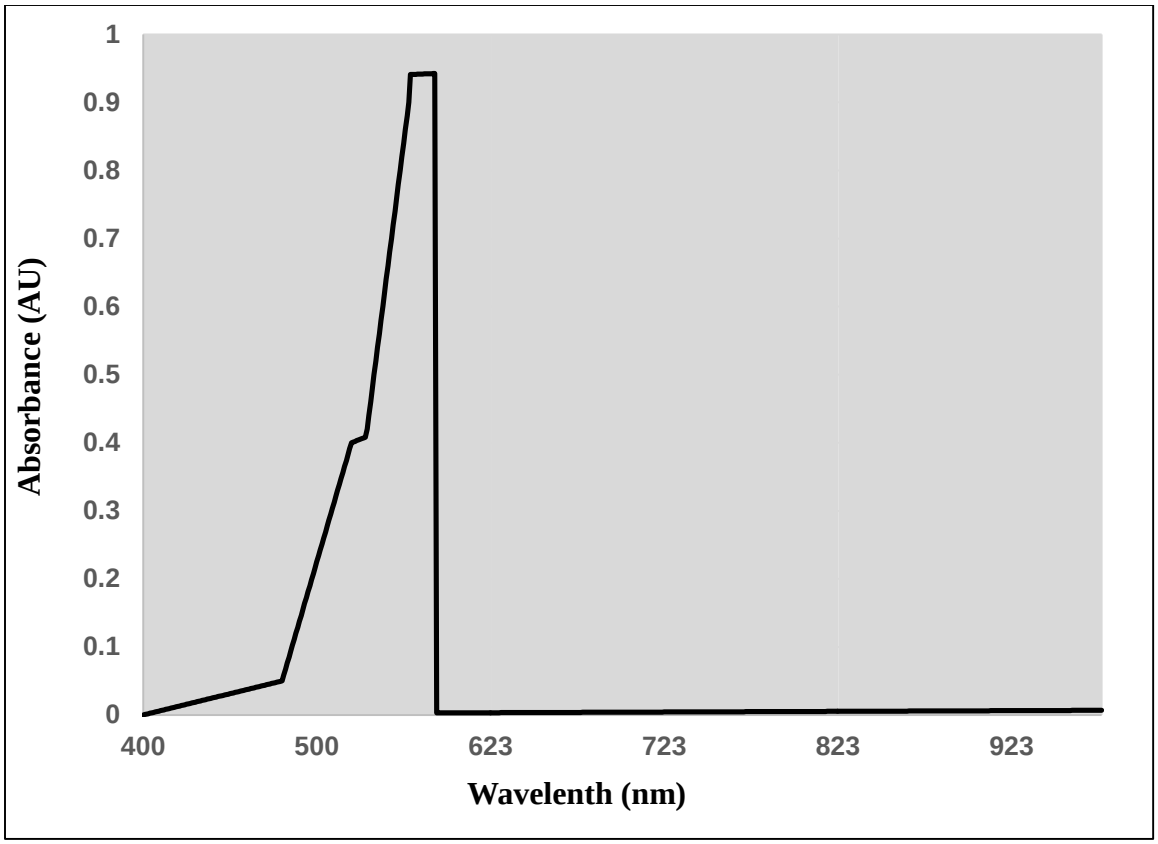


Figure 4.1: Absorbance UV spectrum of Rose Bengal dye (In Water).

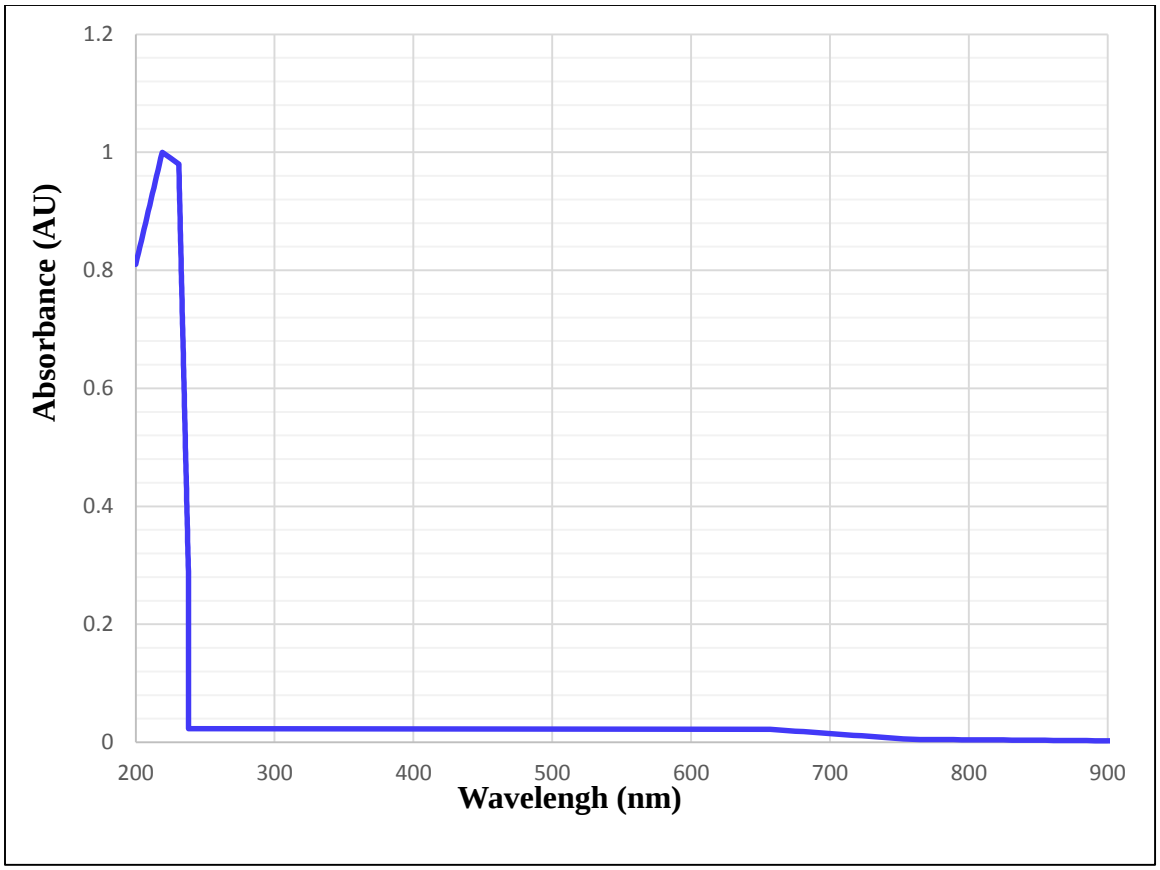


Figure 4.2: Absorbance UV spectrum of Graphene Oxide (In Water).

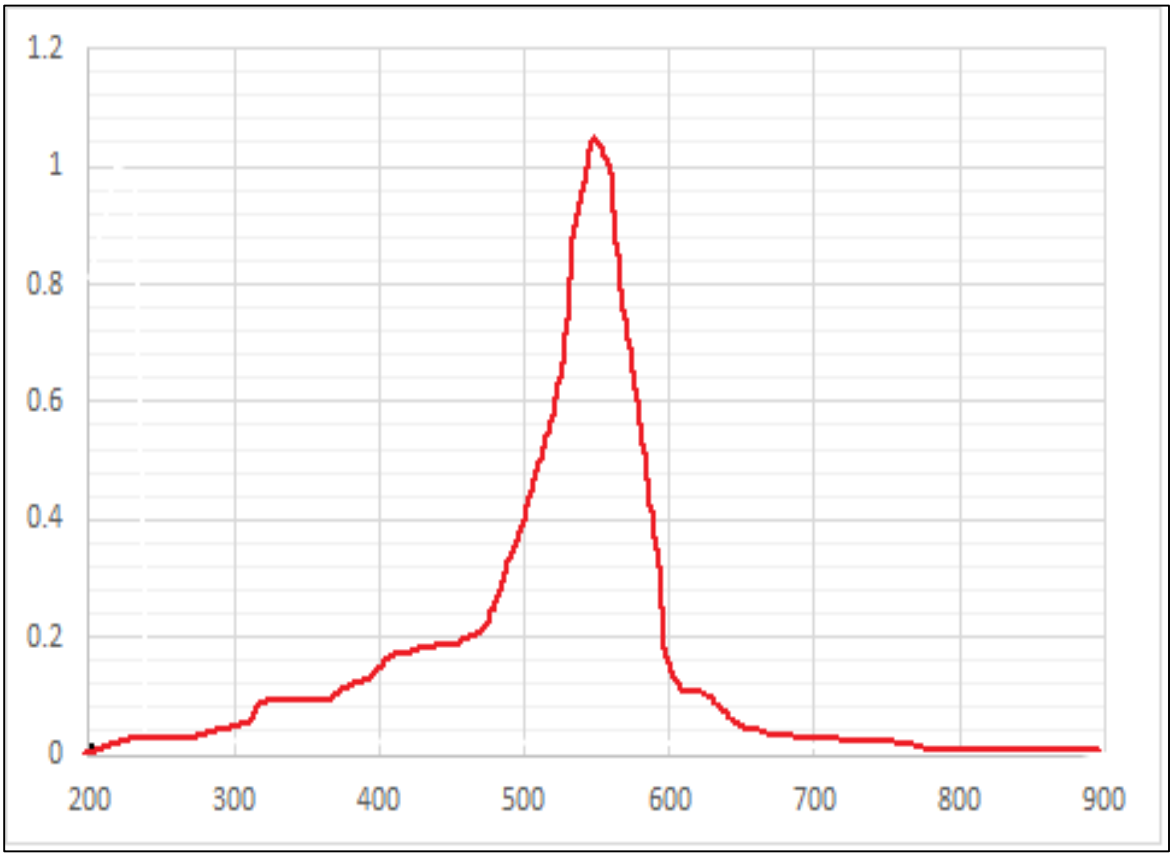


Figure 4.3: Absorbance UV spectrum of Eosin Y dye (In methanol).

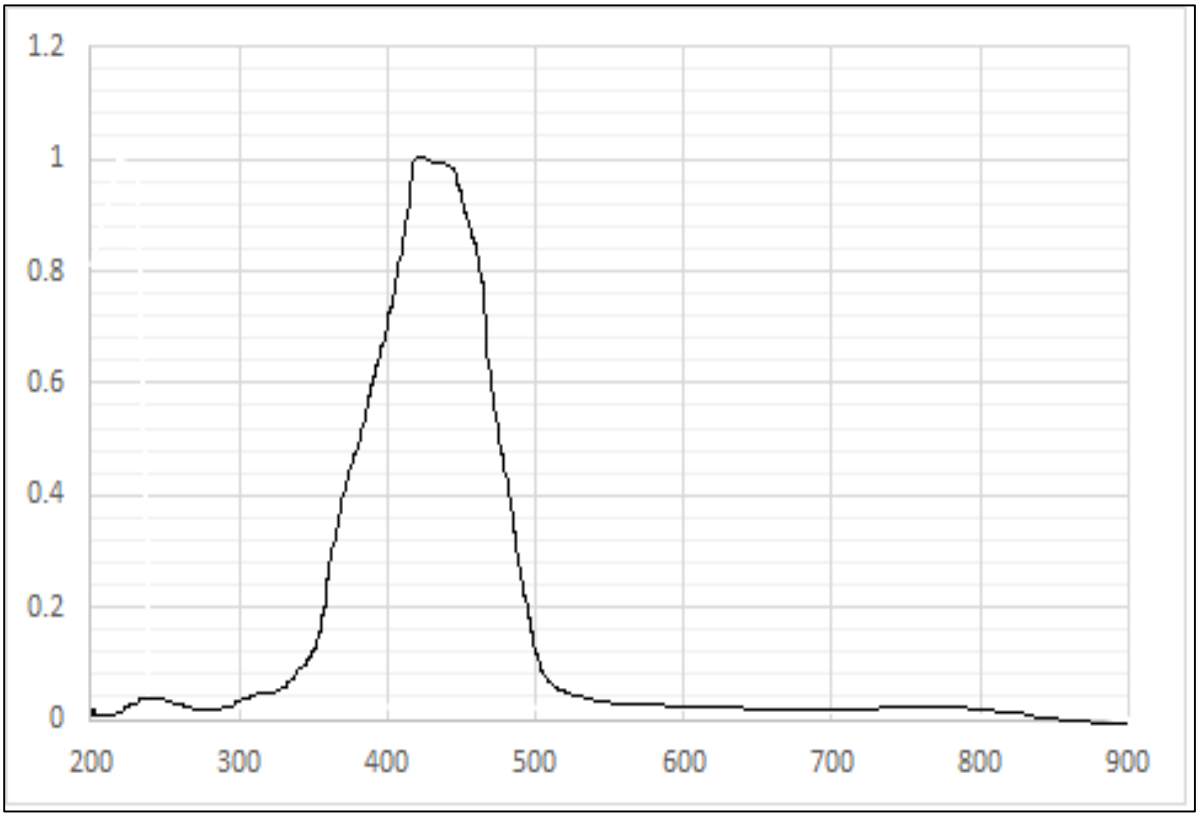
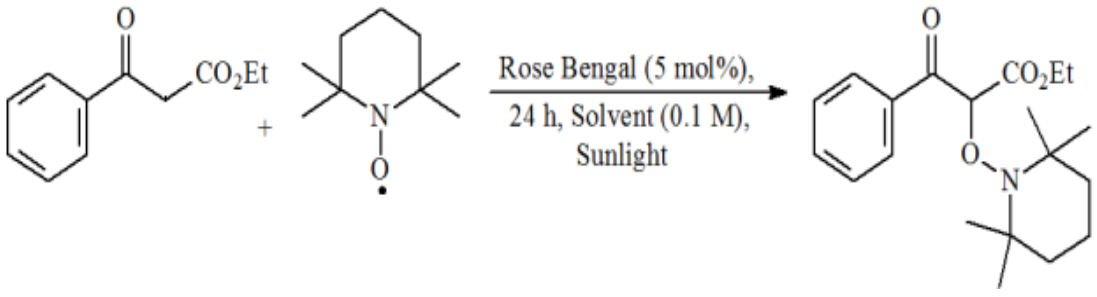


Figure 4.4: Absorbance UV spectrum of Fluorescein dye (In methanol).

4.1 Organic Synthesis of α-Oxyamination reactions

Ethylbenzoyacetate was chosen as an example of α-oxyamination reaction to test the efficiency of our experimental setup by reacting it with TEMPO in the presence of organic dye rose bengal as green catalyst irridated by sunlight in three different solvents (Acetonitrile, Dichloromethane and Water) as illustrated on Figure 4.5, 4.6 and 4.7 respectively. We have achieved 90.9% yield in acetonitrile solvent in only 10 hrs, dichlormetane solvent has shown the least yield of 33.5% in 24hrs however, with 50% yield improvement by the use of the flow reactor. The remarkable yield was obtained in water with 83% yield in only 5 hrs time and with 27.4% yield improvement with the use of the flow reactor. The conversion and product yield result is similar to result obtained by liu and his team who used home fluorescent bulb without a flow reactor (Liu et al., 2010) however, remarkable yield improvement has been recorded in this study with the use of flow reactor. The product NMR spectra are shown in (Figure 4.9 and Figure 4.10)



1a **1b** **1c**

Table 4.1 α-Oxyamination reactions

Reaction	**Dye**	**Solvent**	**Time (hr)**	**Coversion Rate (%)**
Ethylbenzoylacetate + TEMPO	Rose Bengal	Acetonitrile	24	95
Ethylbenzoylacetate + TEMPO	Rose Bengal	Dichlromethane	24	35
Ethylbenzoylacetate + TEMPO	Rose Bengal	Water	24	89.8
Ethylbenzoylacetate + TEMPO	Eosin Y	Water	24	70
Ethyl(4-fluorobenzoyl) acetate+ TEMPO	Rose Bengal	Water	19	89

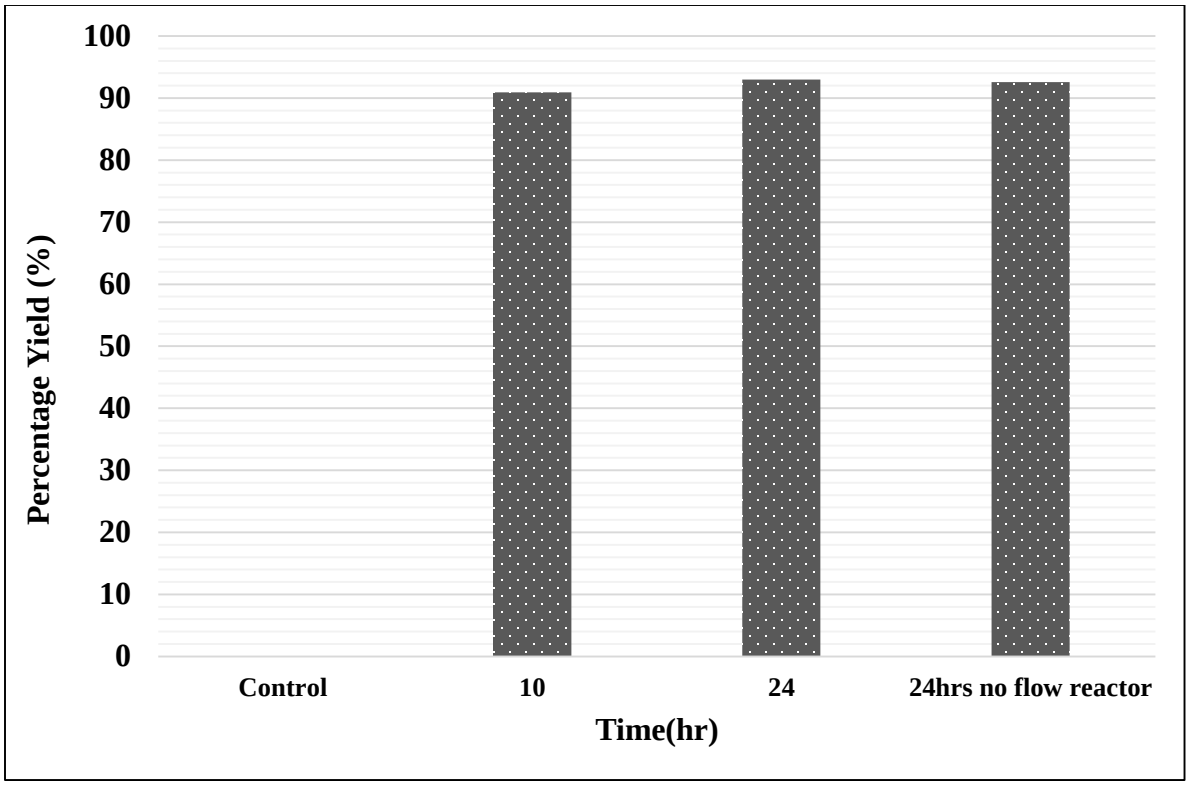


Figure 4.5: α-Oxyamination reactions between ethylbenzoylacetate and (2,2,6,6-Tetramethylpiperidin-1-yl)oxy in the presence of rose bengal organic dye in Acetonitrile solvent.

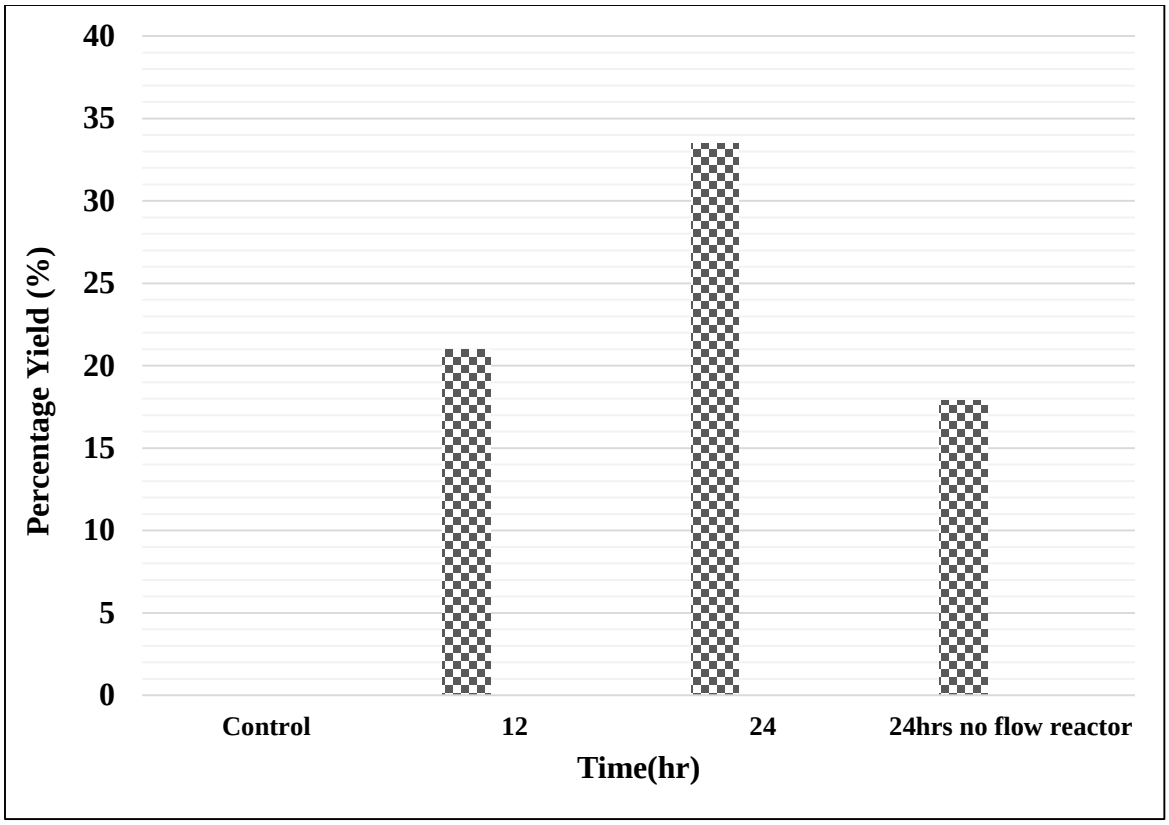


Figure 4.6: α-Oxyamination reactions between ethylbenzoylacetate and (2,2,6,6-Tetramethylpiperidin-1-yl)oxy in the presence of rose bengal organic dye in dichloromethane solvent.

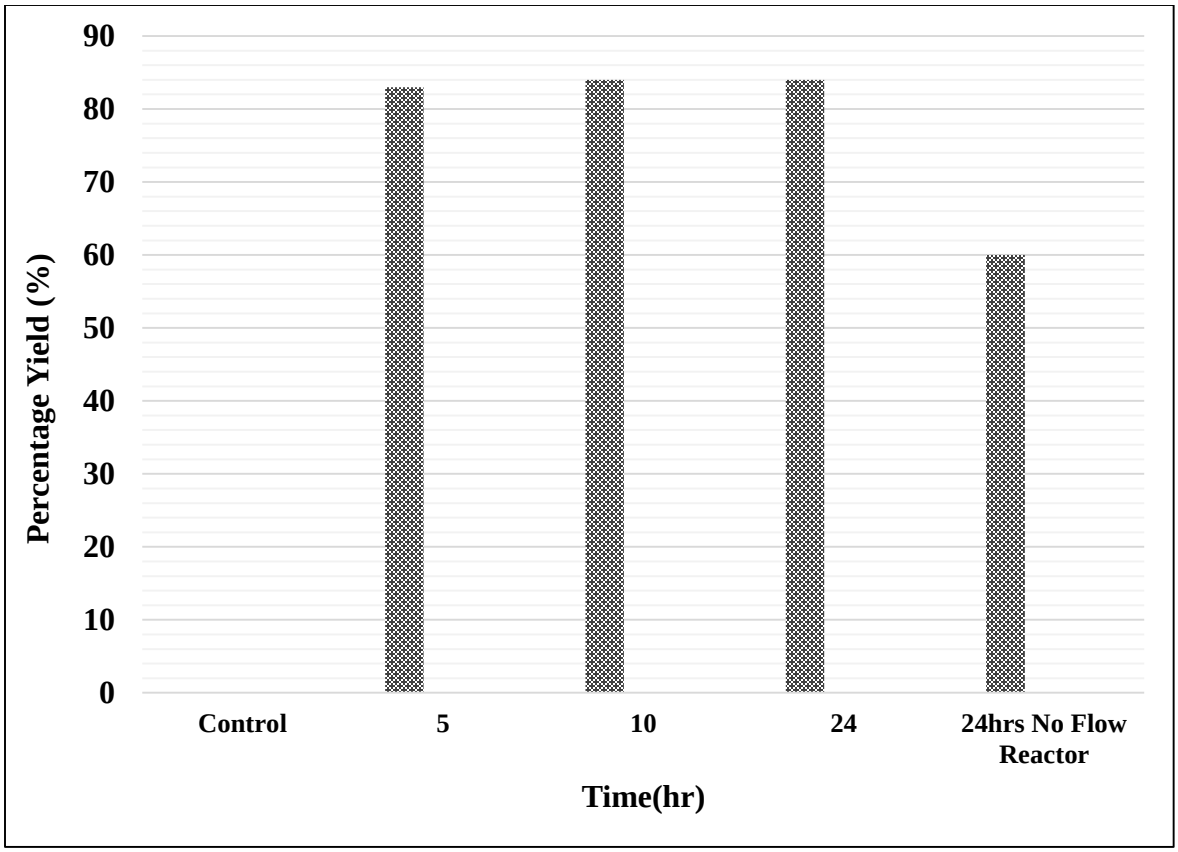


Figure 4.7: α-Oxyamination reactions between ethylbenzoylacetate and (2,2,6,6-Tetramethylpiperidin-1-yl)oxy in the presence of rose bengal organic dye in Water solvent.

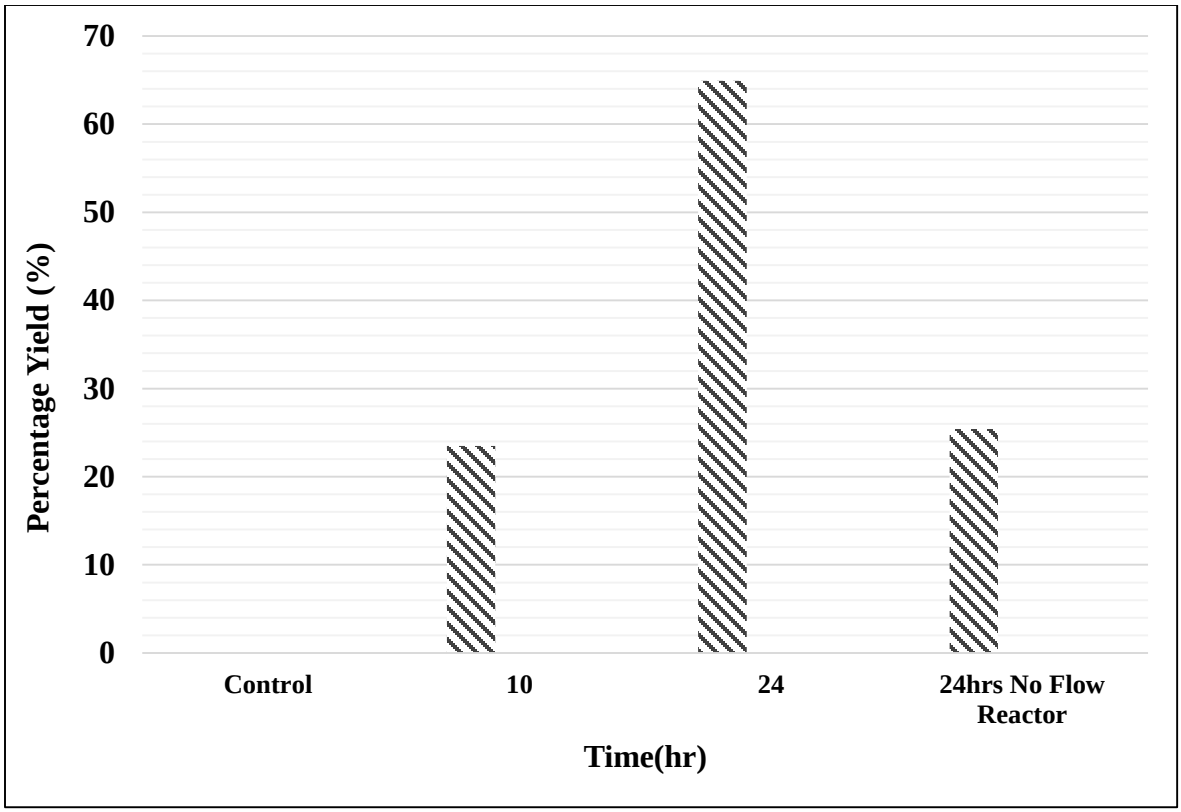


Figure 4.8: α-Oxyamination reactions between ethylbenzoylacetate and (2,2,6,6-Tetramethylpiperidin-1-yl)oxy in the presence of eosin Y organic dye in Water solvent.

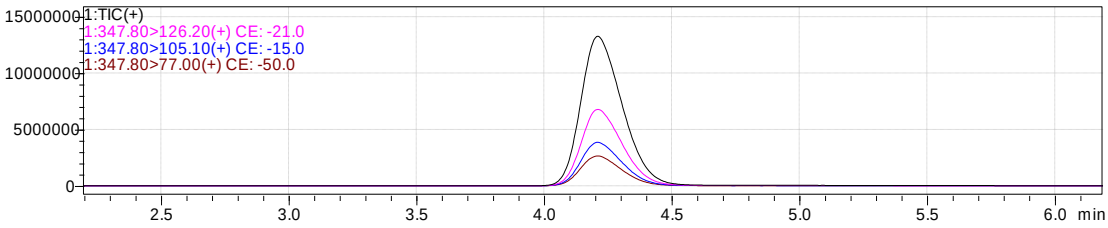


Figure 4.8.1: LCMS spectrum after 10 hours product yield of α-Oxyamination reactions between Ethylbenzoylacetate and (2,2,6,6-Tetramethylpiperidin-1-yl)oxy in the presence of Eosin Y organic Dye in Water solvent.

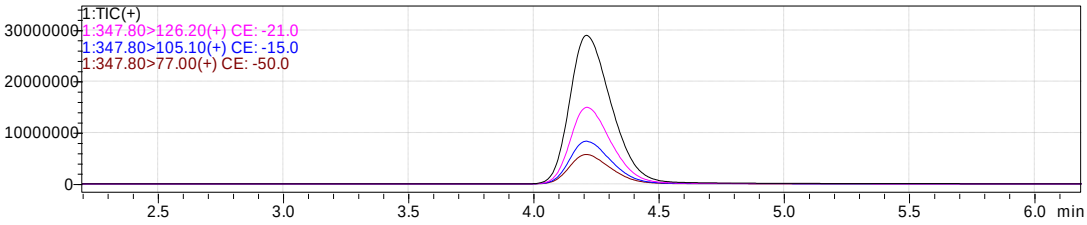


Figure 4.8.2: LCMS spectrum after 24 hours product yield of α-Oxyamination reactions between Ethylbenzoylacetate and (2,2,6,6-Tetramethylpiperidin-1-yl)oxy in the presence of Eosin Y organic Dye in Water solvent.

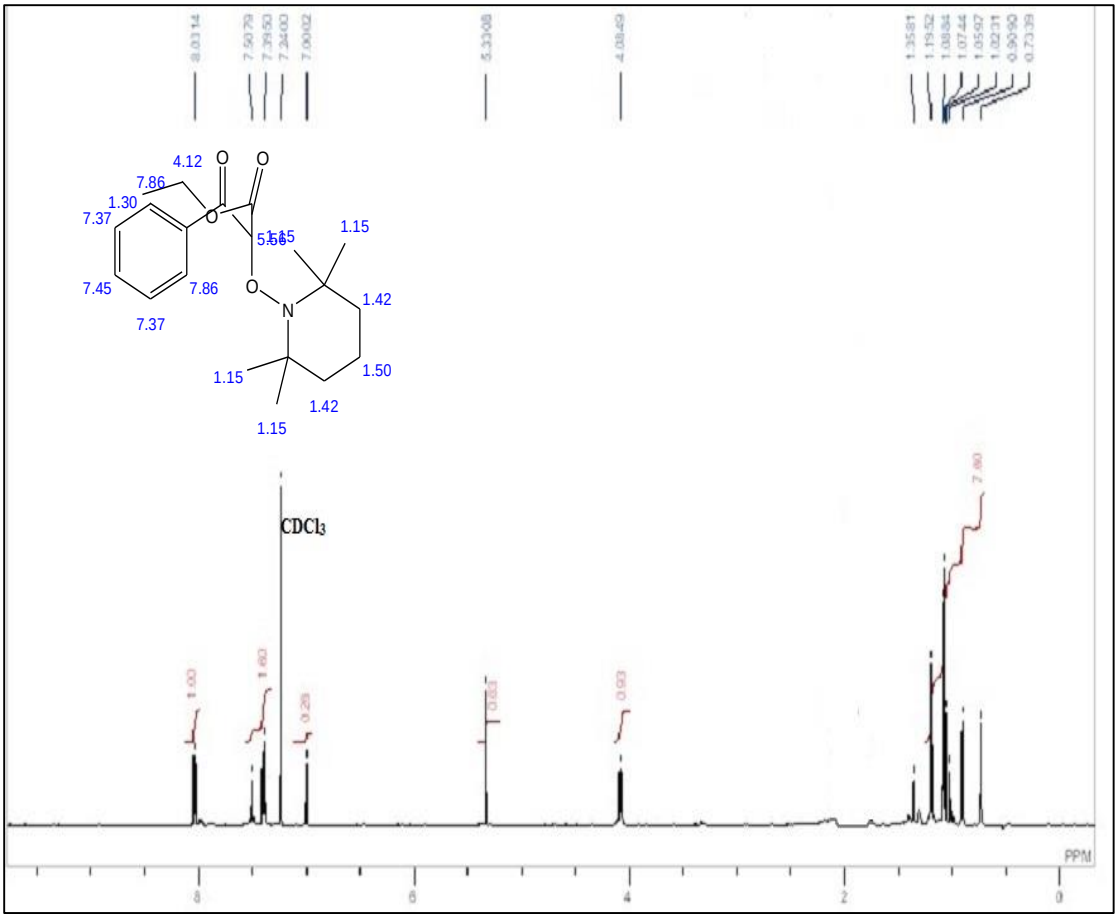


Figure 4.9: ^{1}HNMR of product 1c

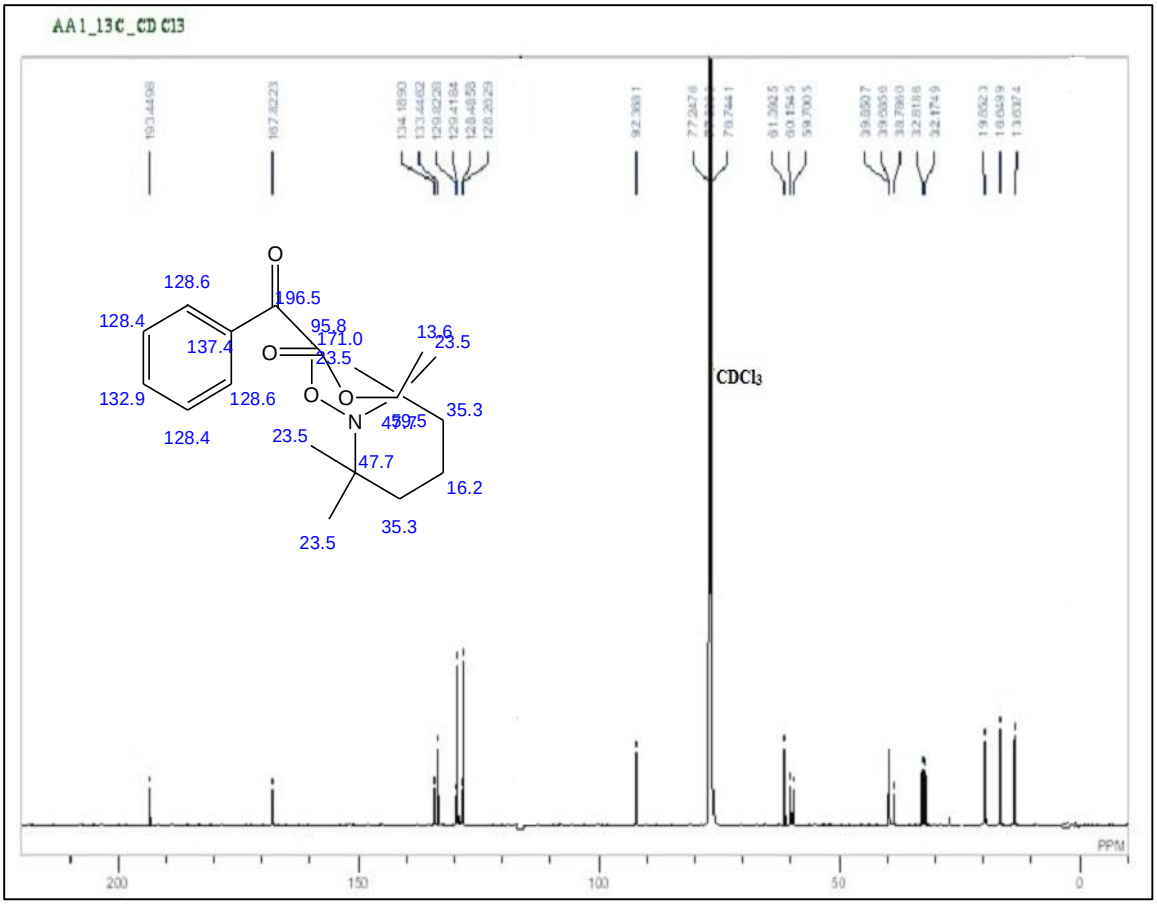
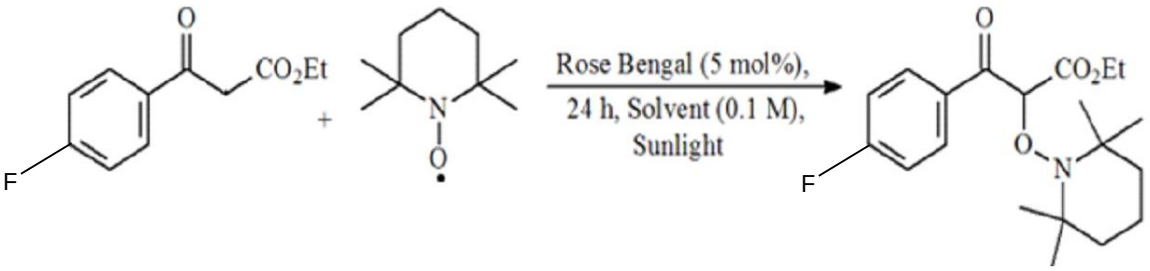


Figure 4.10: ^{13}C NMR of product 1c

We have substituted the hydrogen of the ethylbenzoylacetate with floro group using rose bengal organic dye and we have obtained product yield of 77.5% in 10 hours, 82.5% in 19 hours with 18.2% yield improvement in water with the use of flow reactor. The result is compared with work done by (Liu et al., 2010) which have reported 67% yield in 19 hours in acetonitrile solvent. The product NMR spectra are shown in (Figure 4.12 and Figure 4.13). The structure of all the products were confirmed with nuclear magnetic resonance (1H and 13C NMR) and both liquid chromatography mass spectrometer (LCMS) and high performance liquid chromatography (HPLC) were used for product quantification and conversion rate.



2a **2b** **2c**

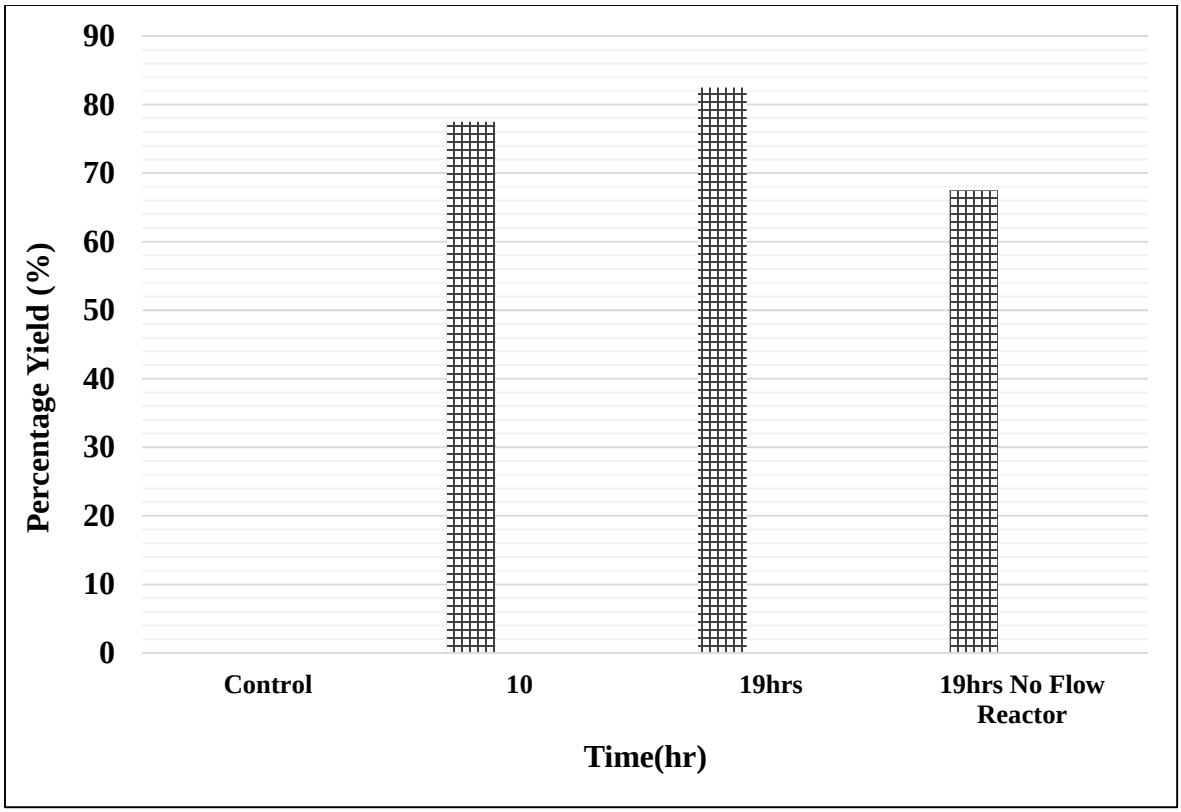


Figure 4.11: α-Oxyamination reactions between ethyl (4-fluorobenzoyl) acetate and (2,2,6,6-Tetramethylpiperidin-1-yl)oxy in the presence of rose bengal organic dye in Water solvent.

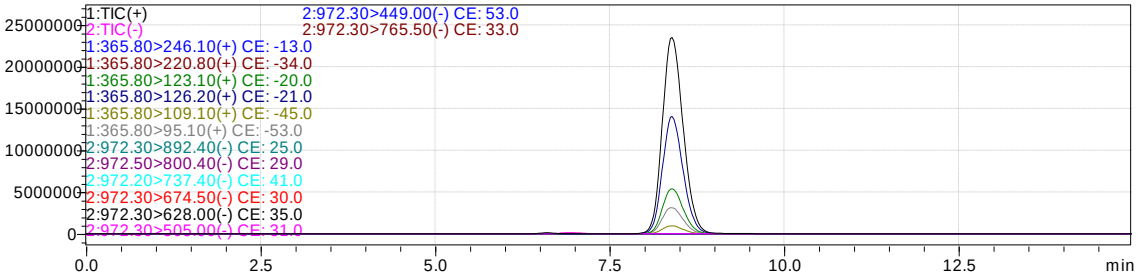


Figure 4.11.1: LCMS spectrum after 10 hours product yield of α-Oxyamination reactions between Ethyl (4-fluorobenzoyl) acetate and (2,2,6,6-Tetramethylpiperidin-1-yl)oxy in the presence of Rose Bengal organic Dye in Water solvent.

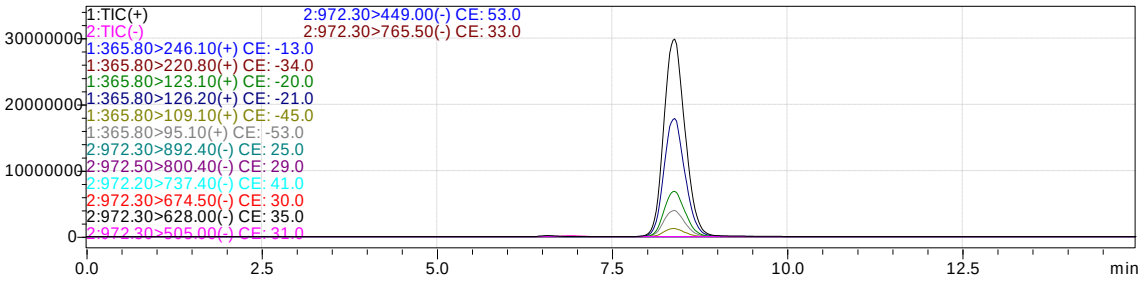


Figure 4.11.2: LCMS spectrum after 24 hours product yield of α-Oxyamination reactions between Ethyl (4-fluorobenzoyl) acetate and (2,2,6,6-Tetramethylpiperidin-1-yl)oxy in the presence of Rose Bengal organic Dye in Water solvent.

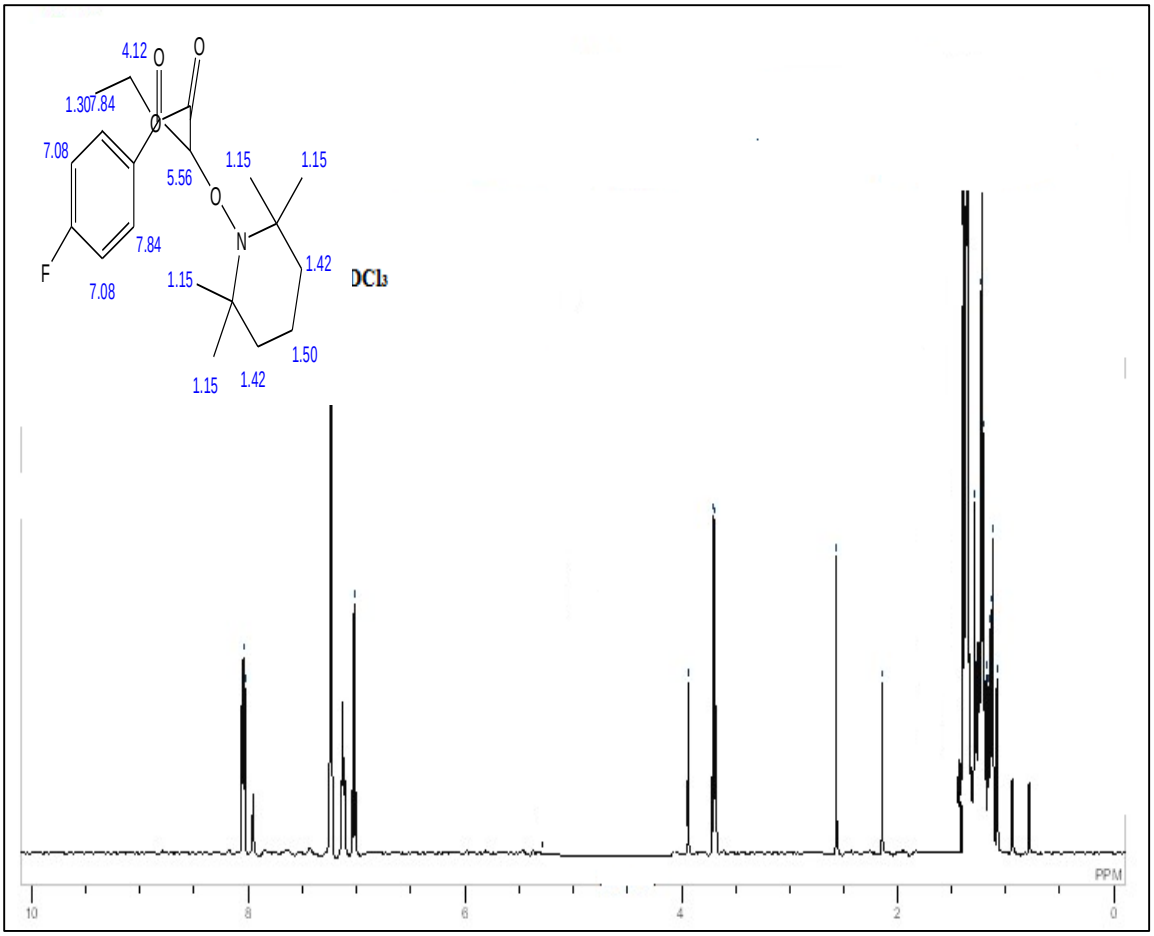


Figure 4.12: ^{1}HNMR of product 2c

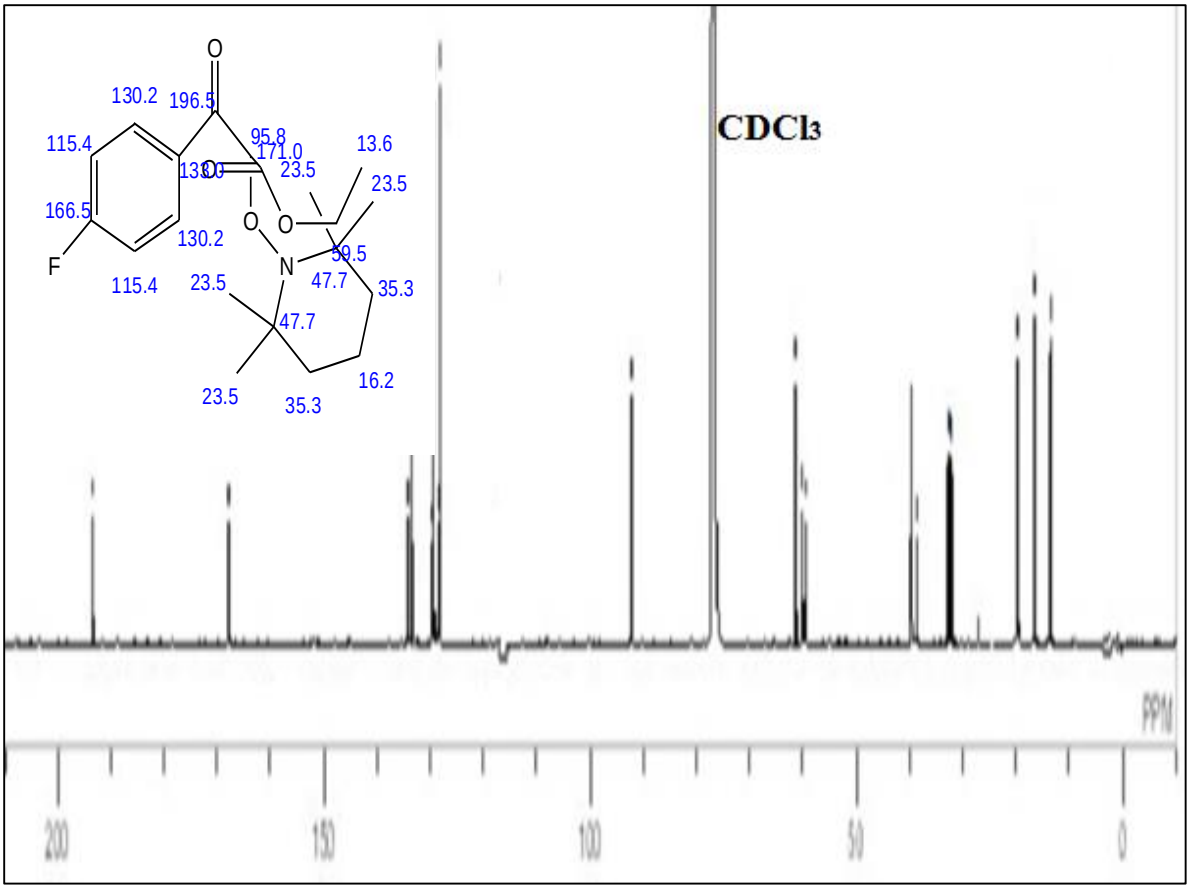
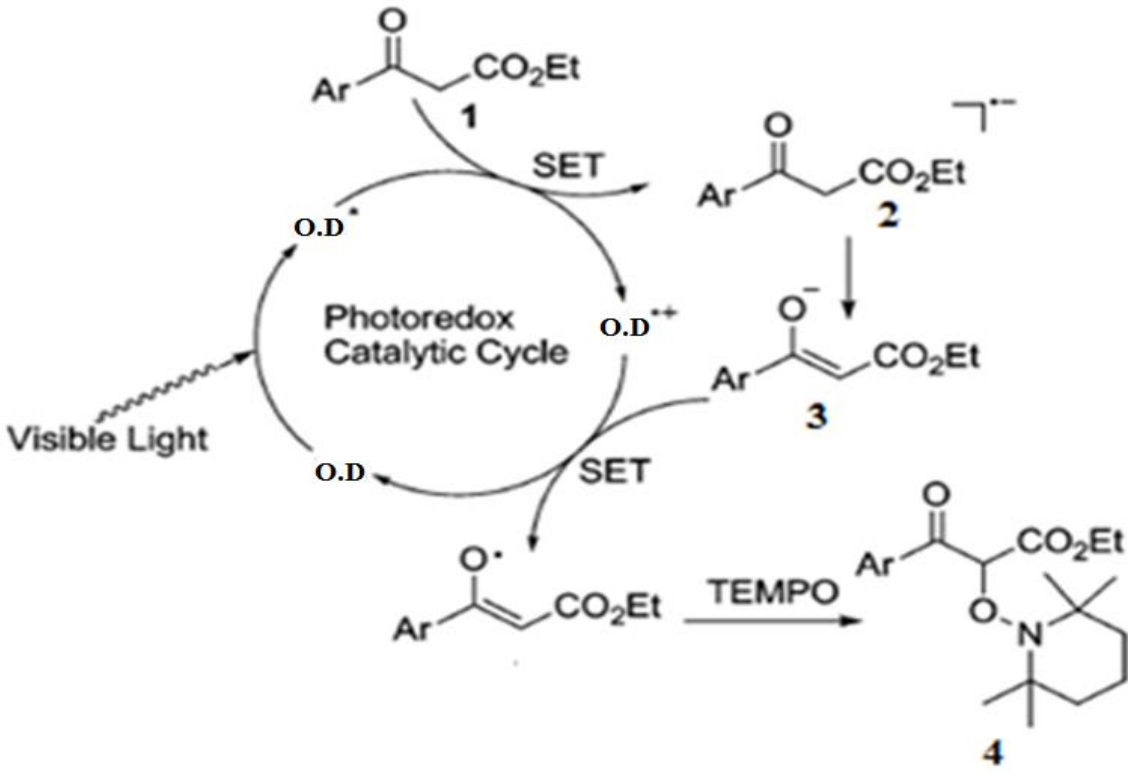


Figure 4.13: ^{13}C NMR of product 2c



Scheme 1

Therefore greatest outcome was achieved using rose bengal organic dye acetonitrile solvent with 90.9% yield in 10 hours (Figure 4.5) however, as a greener approach water has shown excellent yield of 84% with the same organic dye and the same time (Figure 4.7). High yield was noted with the use of flow reactor which is in line with work done by Delville and his group which have reported high yield in the use of continuous flow reactor in azide formation with optimization and scale-up to synthesize explosive compounds (Delville et al., 2011)

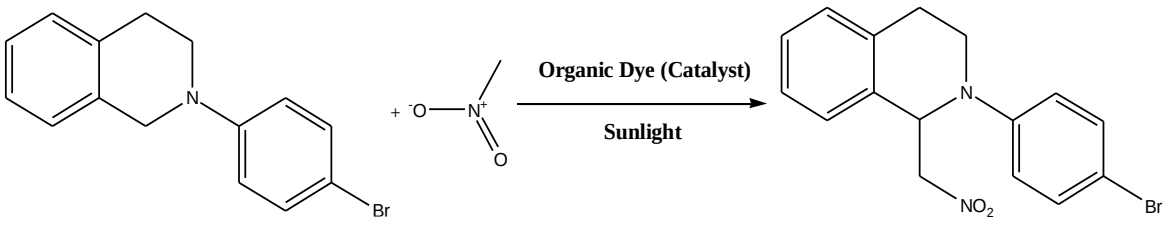
As the mechanism proposed by (Liu et al., 2010) in organic dye photocatalyzed α-oxyamination as shown in scheme 1 above the organic dye (O.D) under visible light is photoexcited and accepts a photon from the sunlight to generate O.D*; as a reductant, it transfers an electron to ethylbenzoylacetate group via a single electron transfer process

(SET). Rose bengal in the mechanism was recycled via another SET process and the radical formed was coupled with free radical TEMPO to give the α-oxyamination reaction product.

4.2 Organic Synthesis of α-Functionalization of tertiary amines.

α-Functionalization of tertiary amines reaction product are important and as a result it is desirable to develop an efficient method for its synthesis. There are other reported techniques like use of green low power light source by Pan and his team (Pan, Kee, Chen, & Tan, 2011).

In this study dehydrogenative reaction is reported where 2-(4-Bromo-phenyl)-1,2,3,4-tetrahydro-isoquinoline and nitromethane in the presence of fluorescein organic dye has yielded 93.8% in 48hours however, excellent yield of 80.9% was achieved in just 24 hours (Figure 4.15) and when the same synthesis was carried out using rose bengal organic dye the yield was found to be 95.1% in 48 hours (Figure 4.14). The result is compared with dehydrogenative coupling reactions catalyzed by rose bengal using visible light irradiation which have reported 95% yield in 48 hours (Pan, Kee, et al., 2011) the NMR spectra of the product are shown in (Figure 4.16 and Figure 4.17)



3a **3b** **3c**

Table 4.2 α-Functionalization of tertiary amines

Dye	**Reactants**	**Time (Hrs)**	**Coversion Rate (%)**
Rose Bengal	Nitromethane + 2-(4-Bromo-phenyl)-1,2,3,4-tetrahydro-isoquinoline	48	100
Fluorescein	Nitromethane + 2-(4-Bromo-phenyl)-1,2,3,4-tetrahydro-isoquinoline	48	99
Rose Bengal	Nitromethane + 2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline	20	98.7
Eoysin Y	Nitromethane + 2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline	24	91

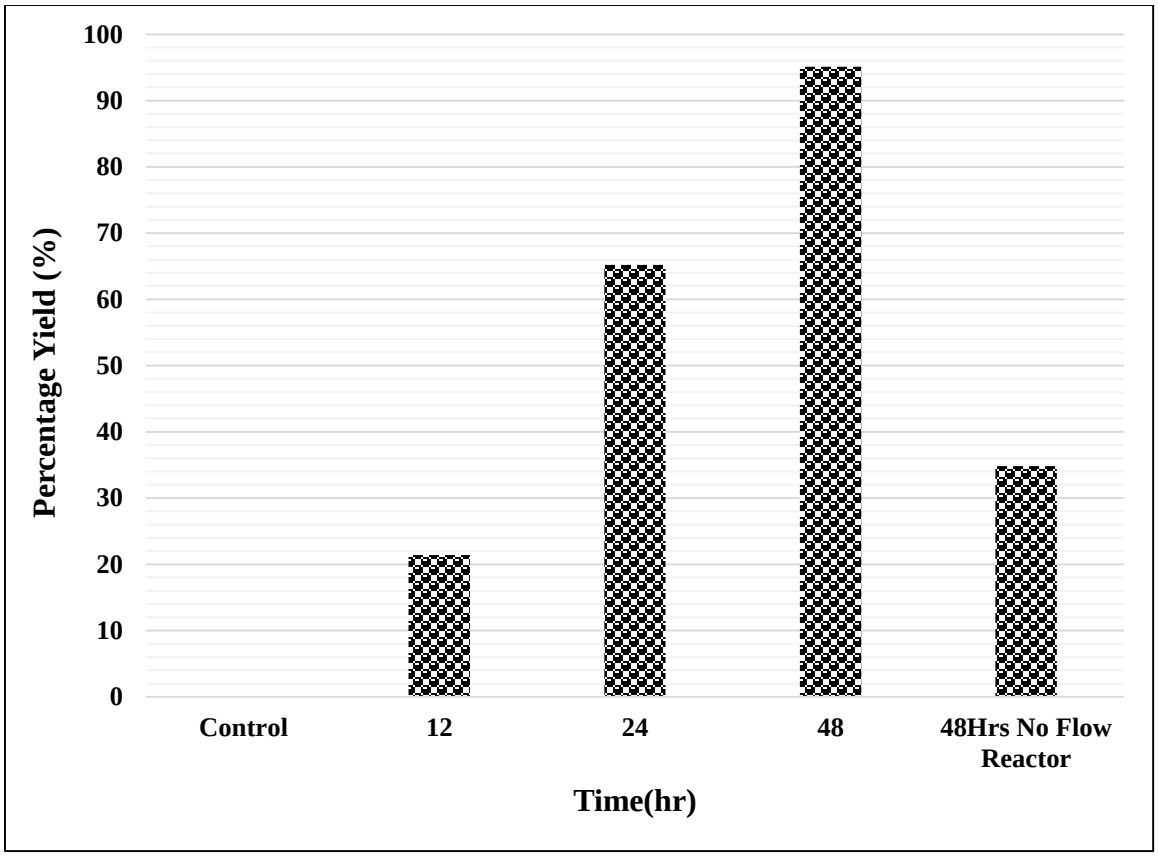


Figure 4.14: α-Functionalization of tertiary amines between 2-(4-Bromo-phenyl)-1,2,3,4-tetrahydro-isoquinoline and nitromethane in the presence of rose bengal organic dye.

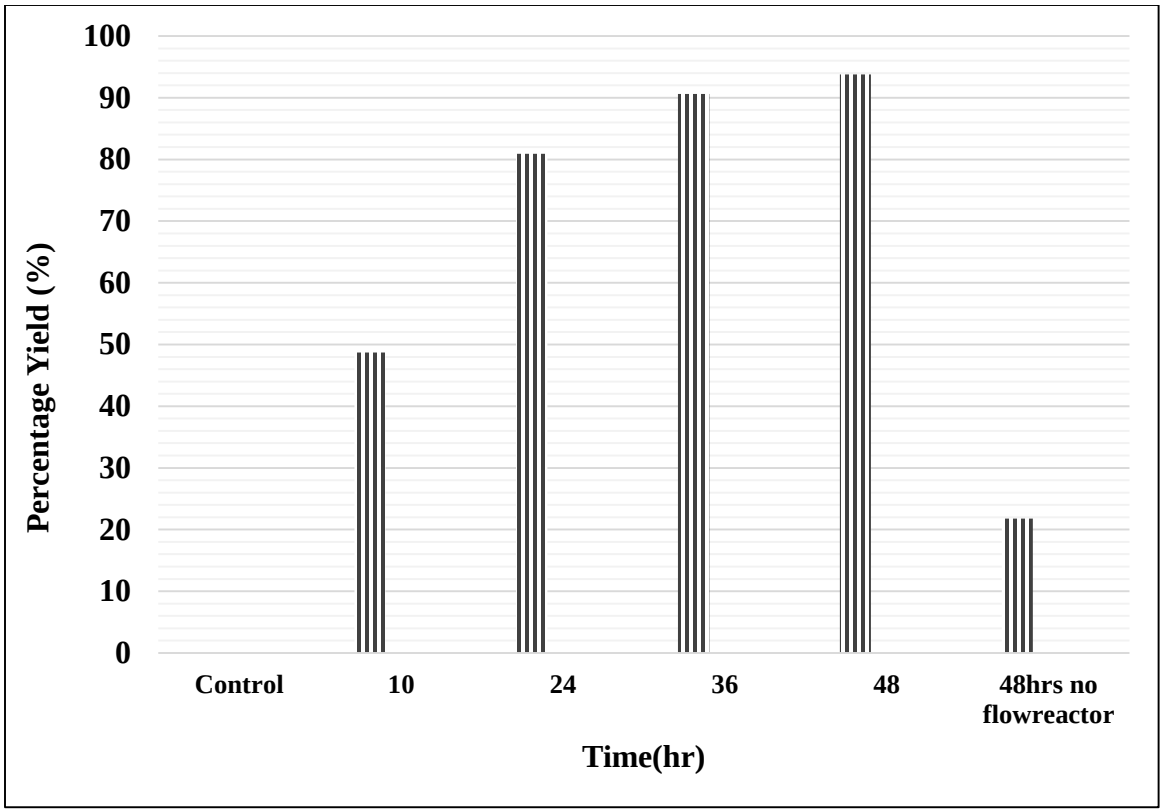


Figure 4.15: α-Functionalization of tertiary amines between 2-(4-Bromo-phenyl)-1,2,3,4-tetrahydro-isoquinoline and nitromethane in the presence of fluorescein organic dye.

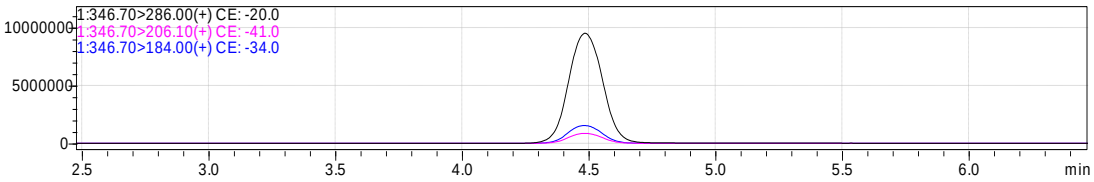


Figure 4.15.1: LCMS spectrum after 24 hours product yield of α-Functionalization of tertiary amines between 2-(4-Bromo-phenyl)-1,2,3,4-tetrahydro-isoquinoline and Nitromethane in the presence of Fluorescein organic Dye.

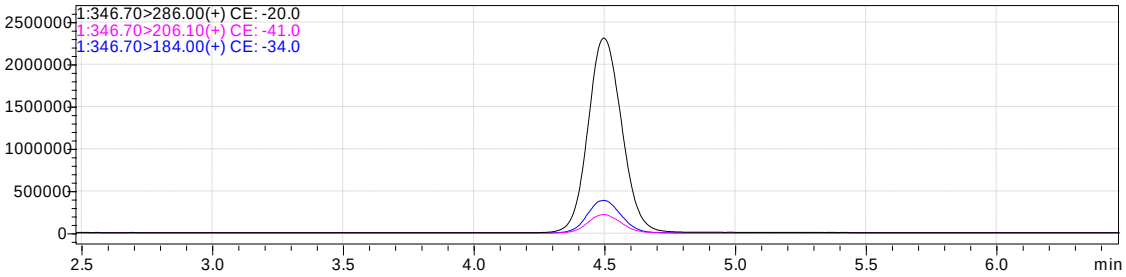


Figure 4.15.2: LCMS spectrum without flow reactor after 24 hours product yield of α-Functionalization of tertiary amines between 2-(4-Bromo-phenyl)-1,2,3,4-tetrahydro-isoquinoline and Nitromethane in the presence of Fluorescein organic Dye.

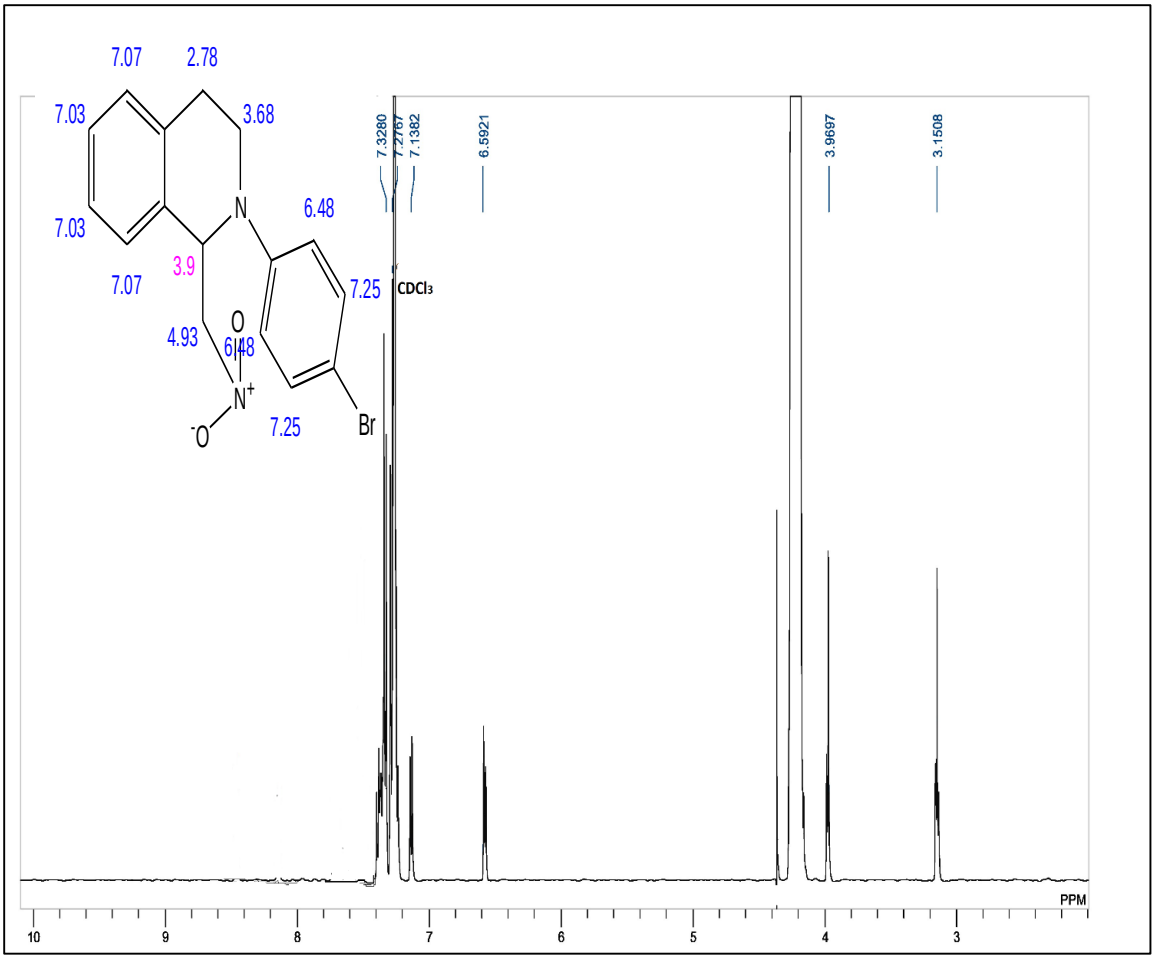


Figure 4.16: ^{1}HNMR of product 2-(4-Bromo-phenyl)-1-nitromethyl-1,2,3,4-tetrahydro-isoquinoline

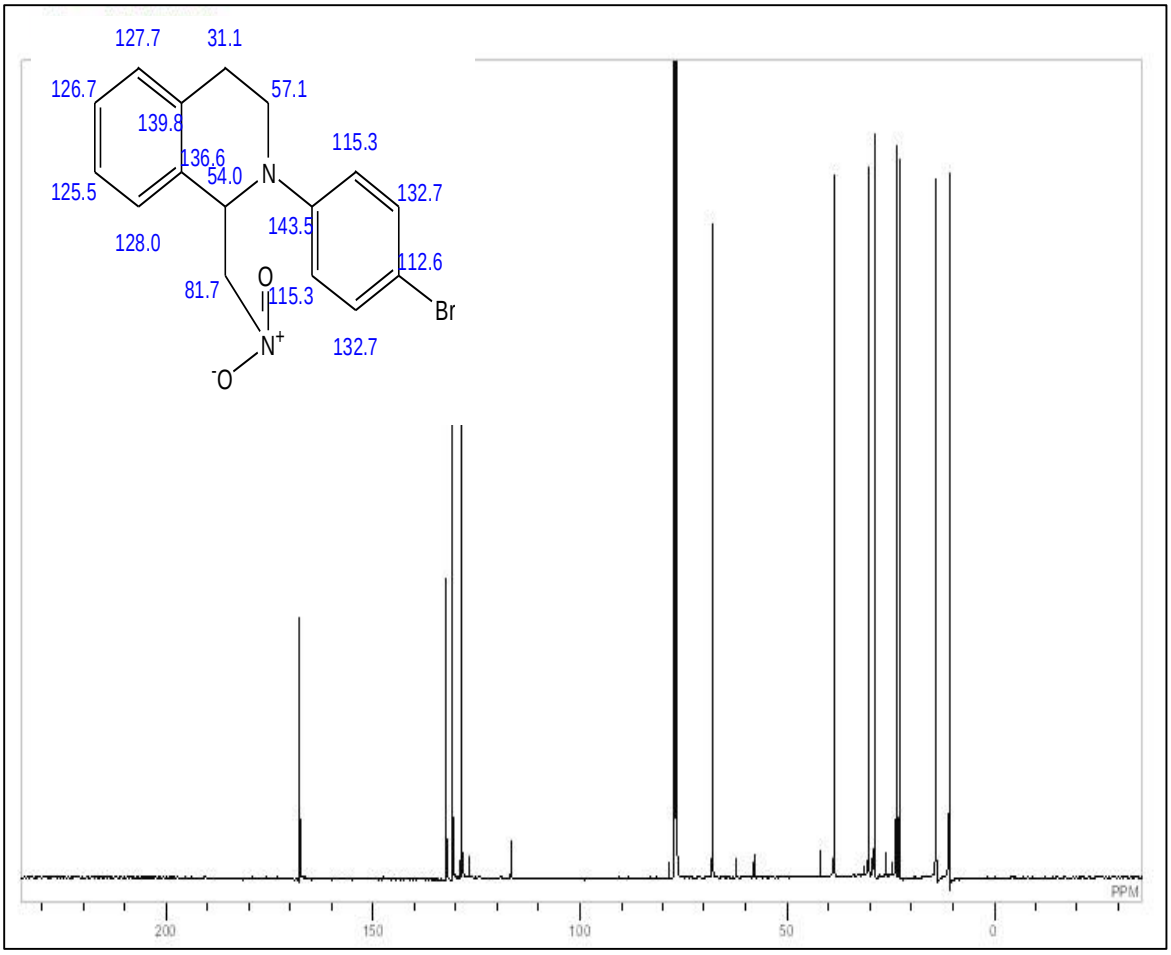
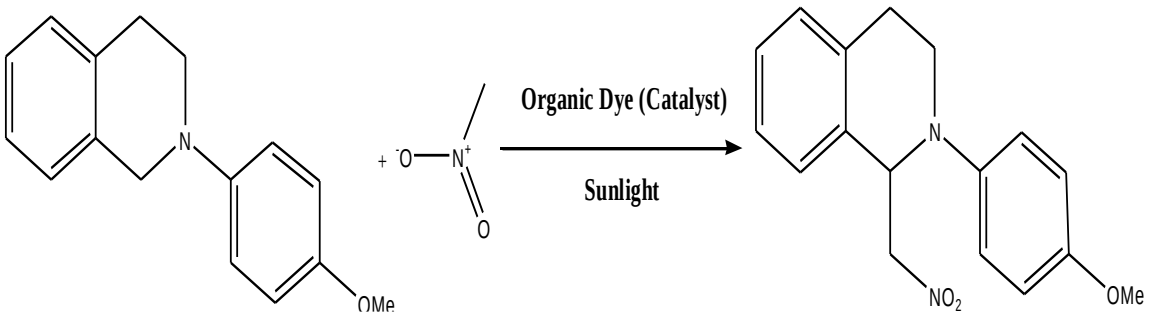


Figure 4.17: ^{13}C NMR of product 2-(4-Bromo-phenyl)-1-nitromethyl-1,2,3,4-tetrahydro-isoquinoline

In this study we have also investigated α-functionalization of tertiary amines between 2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline and nitromethane in the presence of rose bengal organic dye and we have recorded 93.6% yield in 20 hours however good result of 75.1% was obtained in 10 hours. We have also noted low yield of 45.3% without flow reactor (figure 4.18). When the rose bengal was replaced with eosin y organic dye 85.1% yield was obtained with 42.1% yield without flow reactor (Figure 4.19). The NMR spectra of the product is shown in (Figure 4.20 and Figure 4.21)



4a **4b** **4c**

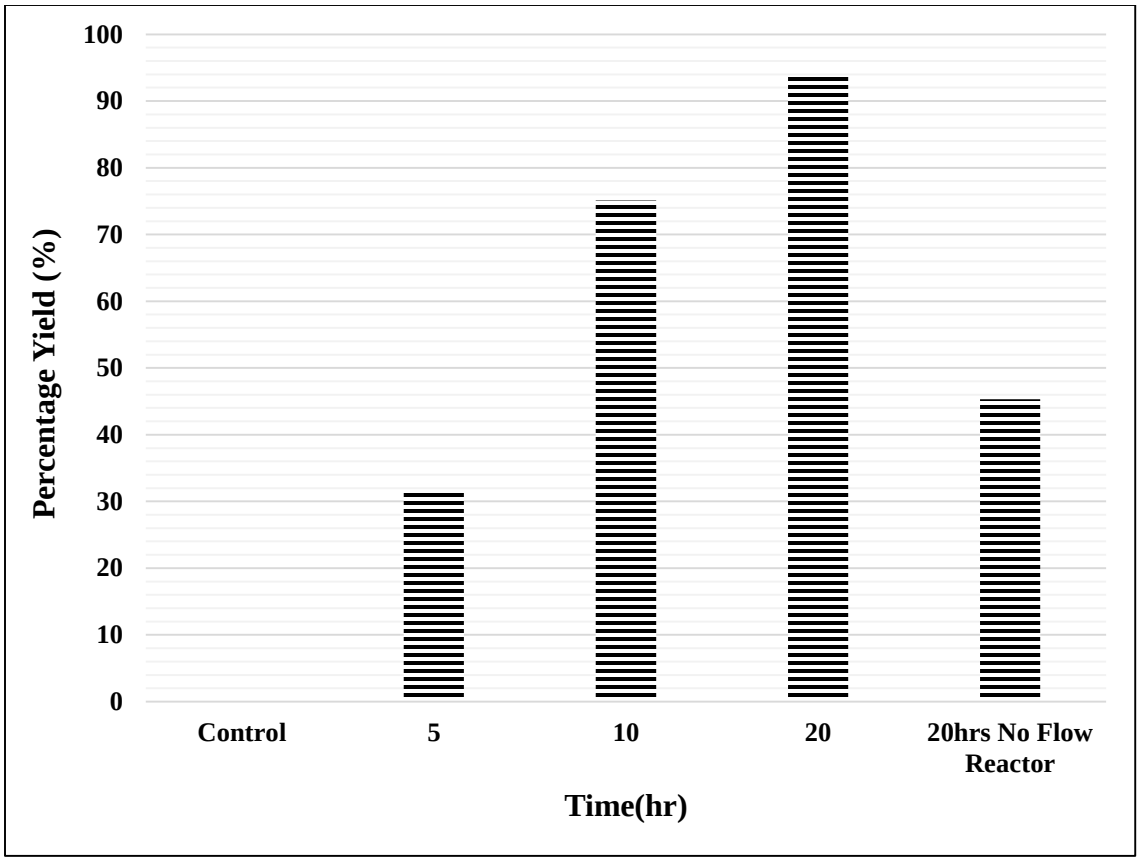


Figure 4.18: α-Functionalization of tertiary amines between 2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline and nitromethane in the presence of rose bengal organic dye.

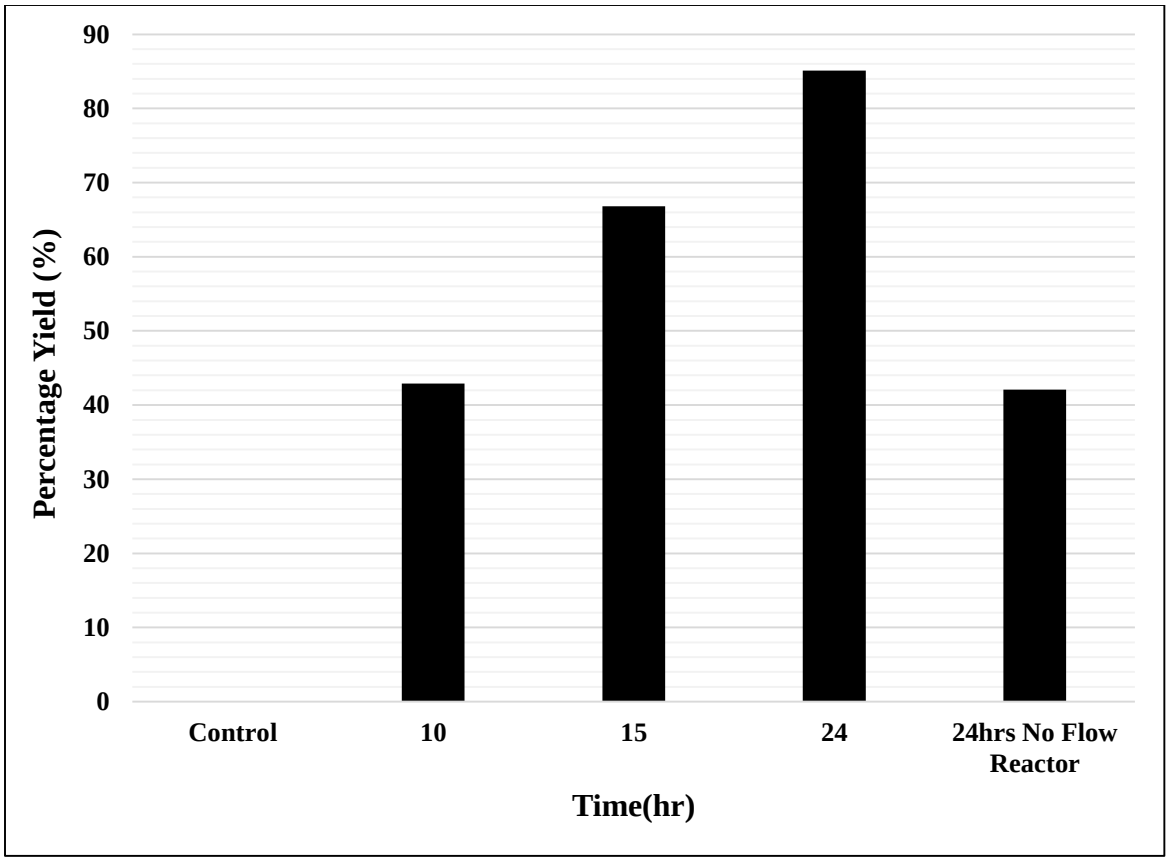


Figure 4.19: α-Functionalization of tertiary amines between 2-(4-Methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline and nitromethane in the presence of eosin Y organic dye.

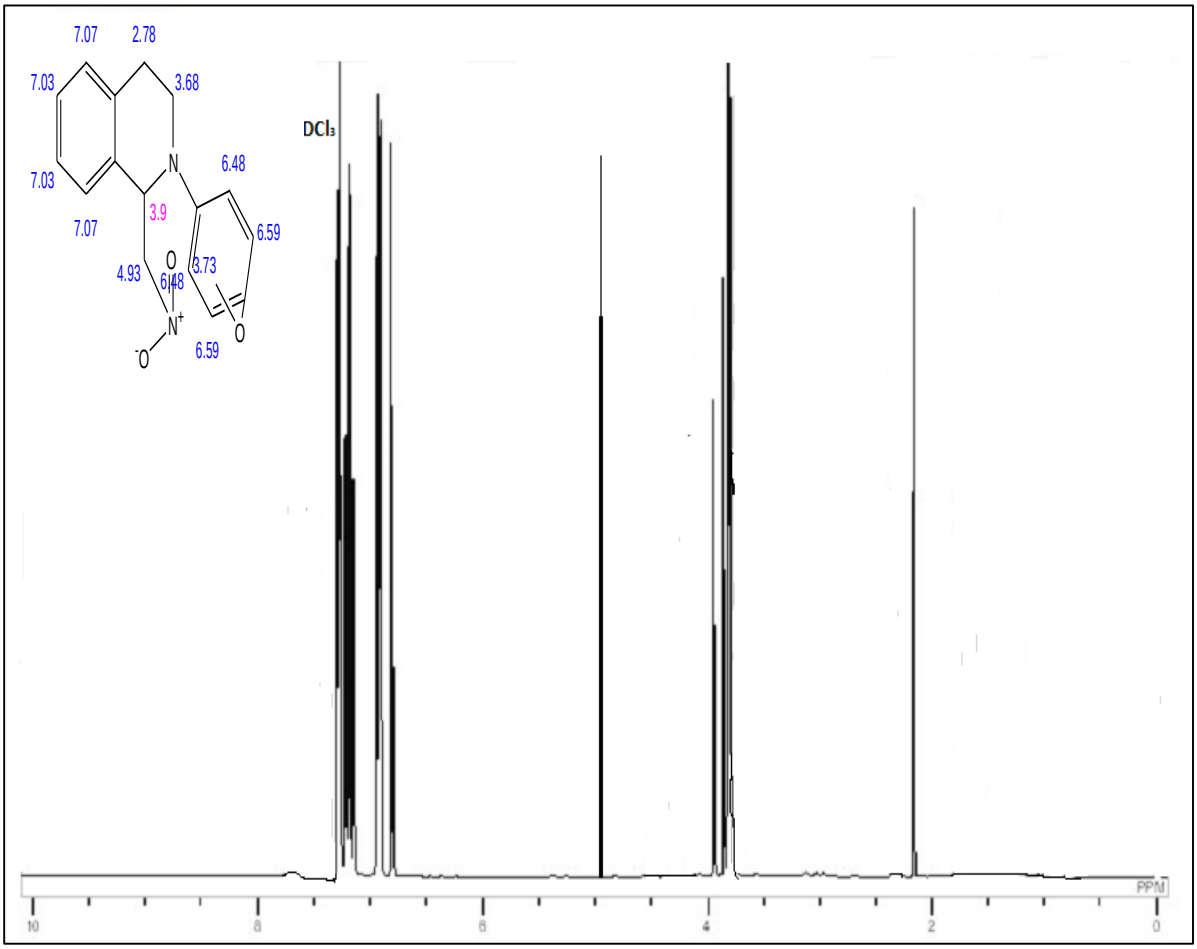


Figure 4.20: ^{1}HNMR of product 2-(4-Methoxy-phenyl)-1-nitromethyl-1,2,3,4-tetrahydro-isoquinoline

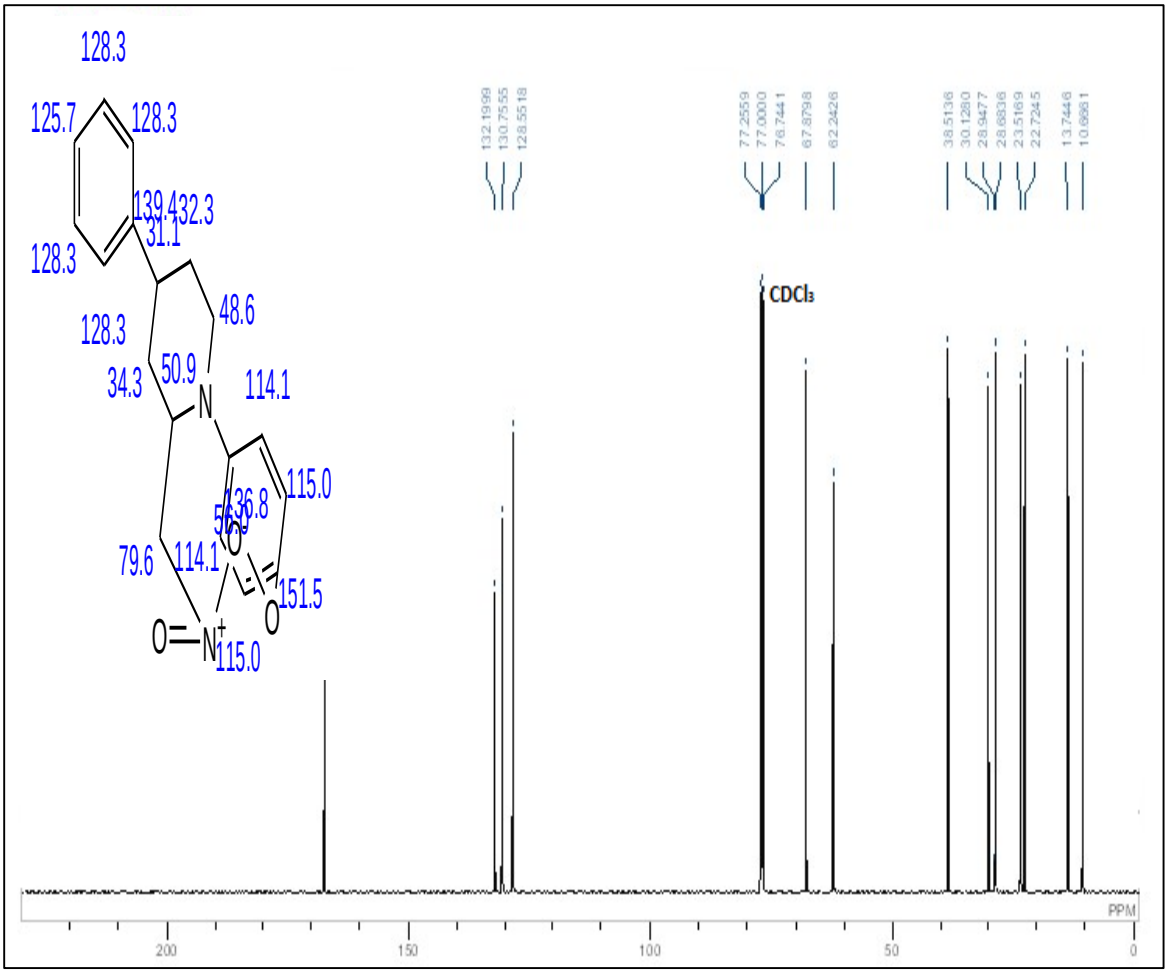
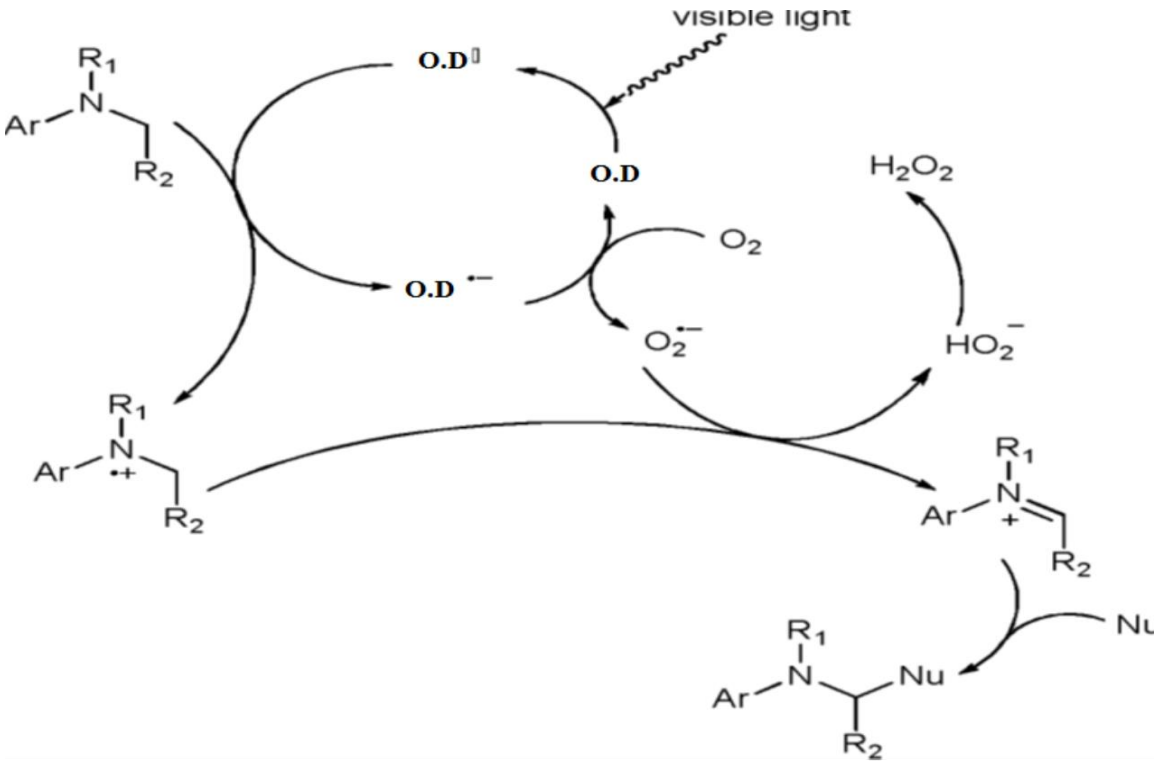


Figure 4.21: ^{13}CNMR of product 2-(4-Methoxy-phenyl)-1-nitromethyl-1,2,3,4-tetrahydro-isoquinoline



Scheme 2

The optimization of α-functionalization of tertiary amines reaction using 2-(4-Bromo-phenyl)-1,2,3,4-tetrahydro-isoquinoline and nitromethane in the presence of rose bengal organic dye has shown the highest yield where 95.1% was achieved in 48 hours (figure 4.14) compared to when fluorescein organic dye which yielded 93.8% in also 48 hours (figure 4.15) and when 2-(4-Methoxy-phenyl)-1-nitromethyl-1,2,3,4-tetrahydro-isoquinoline was used it showed that rose bengal is the best organic dye that has shown higher yields of 93.1% (Figure 4.18) in 20 hours compared to eosin Y organic dye which has shown 85.1% yield in 24 hours (Figure 4.19). High yields recorded with the use of the flow reactor can be attributed to the pump which also sucks air through the capillary tube as air is very essential for the reaction hence, high yield in α-functionalization of tertiary amines with use of flow reactor due to maximum contact between reaction solution and oxygen. The result is in agreement with work done Steen and his team who found that the

use of a continuous flow-reactor employing a mixed hydrogen-liquid flow stream for the efficient reduction of imines to amines (Saaby, Knudsen, & Ley, 2005)

Mechanism was proposed by Pan and his group as shown in scheme 2 (Pan, Kee, et al., 2011) where they proposed that the organic dye goes into excited state when it absorbs visible light radiation, and removes an electron from the tertiary amine group through single electron transfer (SET). After then the organic dye radical anion and goes back to the ground state followed by the formation of iminium after the tertiary amine radical cation gives single hydrogen to the deoxygenated organic dye that could be confined by nucleophiles under normal minor conditions, to give the end product.

$$\textbf{Conversion (\%)} = \frac{[\textbf{Initial Reading}]-[\boldsymbol{Final\ Reading}]}{[\textbf{Initial Reading}]} \times \mathbf{100} \quad \ldots\ldots \text{ i}$$

The conversion rate was calculated using the above expression where initial reading is the concentration of the limiting reactants at the starting time and final reading is the concentration of the limiting reactant that remained at the end of the experiment time.

We have found excellent conversion rate in most cases which is directly propotional to the percentage yield.

4.3 Treatment of phenol from contaminated water using graphene oxide and organic dye rose bengal.

4.3.1 Characterization of graphene oxide

To understand the microstructure, surface morphology and the effect of the treatment process various characterization procedures were performed. The results obtained depicts adsorption characteristics of the graphene oxide. The results attained from the FTIR and the XRD are shown on Figure 4.22 and Figure 4.23 respectively.

4.3.1.1 Brunauer-Emmett-Teller (BET) Surface Area Analysis

The surface of the graphene oxide, that composed of the external and pore areas were achieved giving reliable information to conclude for the effects of surface porosity and particle size of the material. It was noted that the organic dye has better phenol removal capacity which can be attributed to its photocatalytic nature. Following the addition of graphene oxide at different ratios from low dosage to high dosage no significant improvement was recorded.

4.3.1.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FT-IR spectrum of graphene oxide shows a broad absorption peak at around 3444 cm-1 corresponding to -OH from graphene oxide. A peak at 2923.7 cm-1 represents the C-H group. The peak at around 1620 cm-1 is indicative of C-O deformation mode. There are no significant changes in the FT-IR of the graphene oxide. Some peaks slightly shifted to a lower frequency from 3443.9 cm-1 region to 3434 cm-1 (-OH), around 1620.9 cm-1 (C-

H) stretching vibrations in the spectrum. Also it was evident from the figures that there were no significant changes in the spectrum of the material and phenol treated graphene oxide, demonstrating perhaps a physical surface adsorption of the graphene oxide (Figure 4.22).

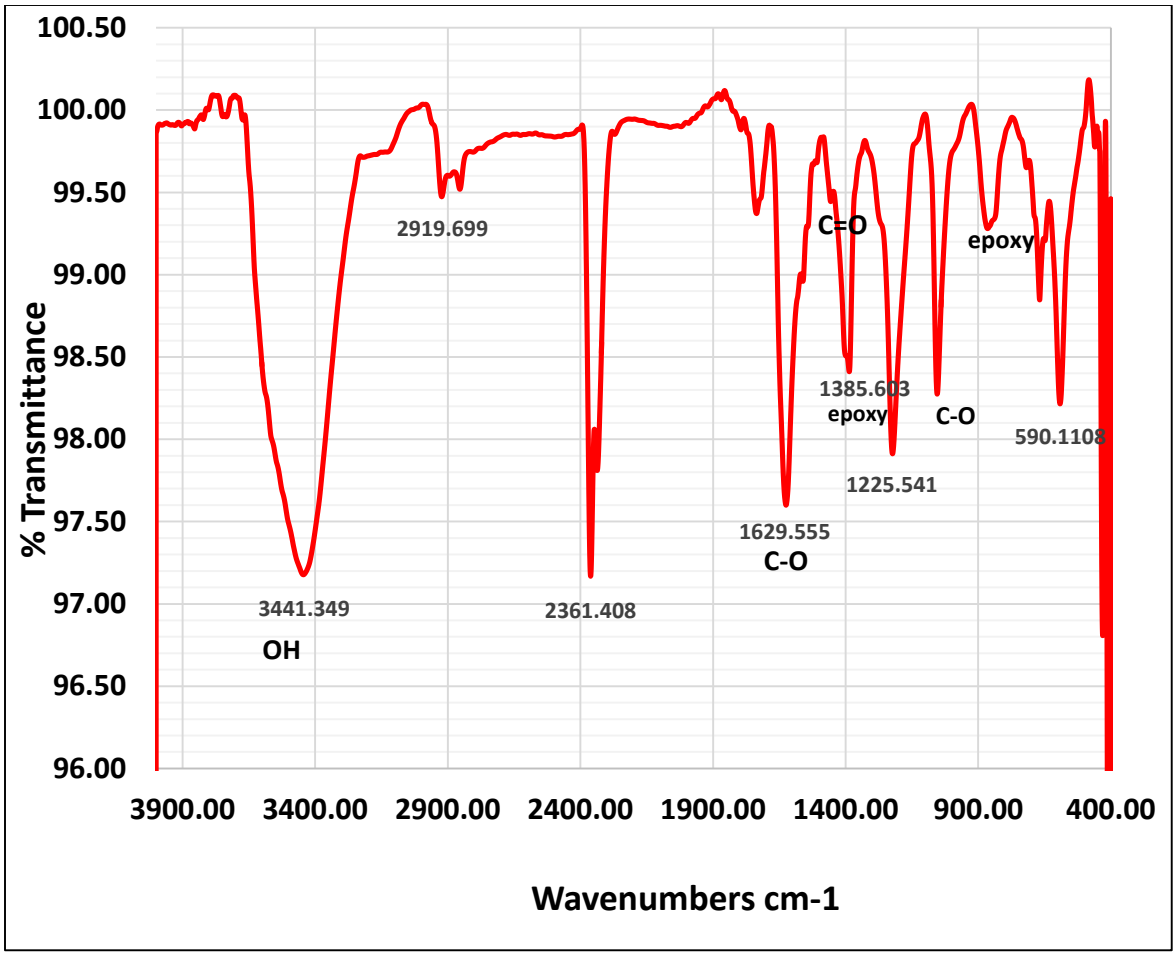


Figure 4.22: FTIR spectrum of the synthesized graphene oxide

4.3.1.1.2 X-Ray Diffraction (XRD)

XRD of graphene oxide is shown on (Figure 4.23) the result shows amorphous phase pattern which are scattered in many directions leading to a large bump distributed in a wide range (2 Theta) instead of high intensity narrower peaks. Since phenol degradation under sunlight irradiation without the organic dye was low compared with the removal by the presence of the organic dye, phenol removal comes predominantly from organic dye photocatalytic degradation. Main part of phenol removal is realized in the first hours of sunlight irradiation afterwards removal increases progressively with increasing irradiation time up to 10 hours in most cases. This result is in consistent with report of Inagaki and his team who have reported same trend on phenol removal from water using TiO_2 (Tryba, Morawski, & Inagaki, 2003)

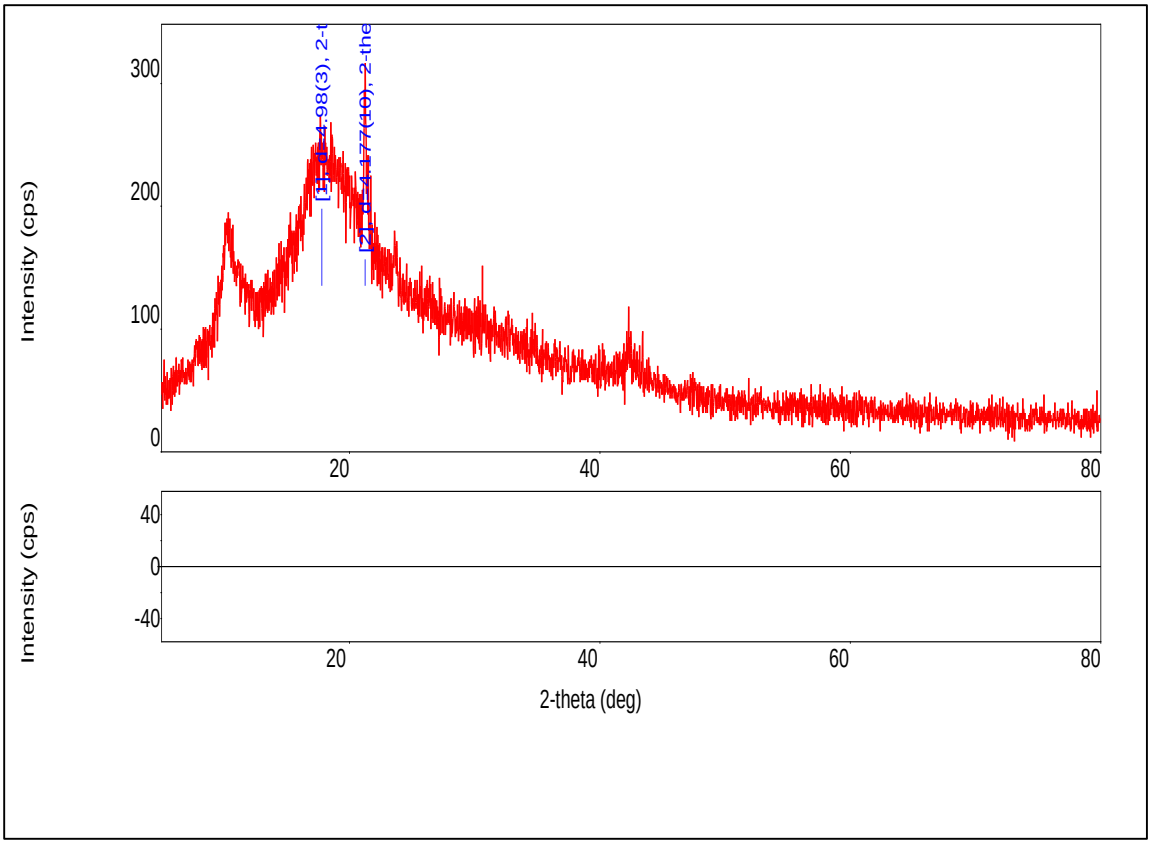


Figure 4.23: XRD spectrum of the synthesized graphene oxide

4.3.2 Blank Batch Experiment Runs

In order confirm the result obtained is directly correlated to the materials used, blank runs were conducted where the deionized water was spiked with phenol and injected to the flow reactor for 10 hours without any graphene oxide nor the organic dye added. The result has shown some of the phenol was removed however, negligible amount which can be attributed to the vigorous stirring and the continuous flow reactor.

Therefore the results reported in this study is directly related to the addition of the graphene oxide and the organic dye accompanied by the efficiency of the flow reactor.

4.3.3 Testing of both graphene oxide and organic dye for phenol Removal

To ascertain the efficiency of graphene oxide and the organic dye on the phenol removal several experiments were conducted to understand each parameter and its effects on the phenol removal from contaminated water. (Figure 4.29) shows that only the organic dye at pH11 brought about notable removal of phenol from the water. However, various combination of the graphene oxide and the organic dyes has shown different remarkable percentage removal. More experiments were conducted on the organic dye alone to obtain the optimum set of experimental conditions for the removal of phenol from the spiked solution.

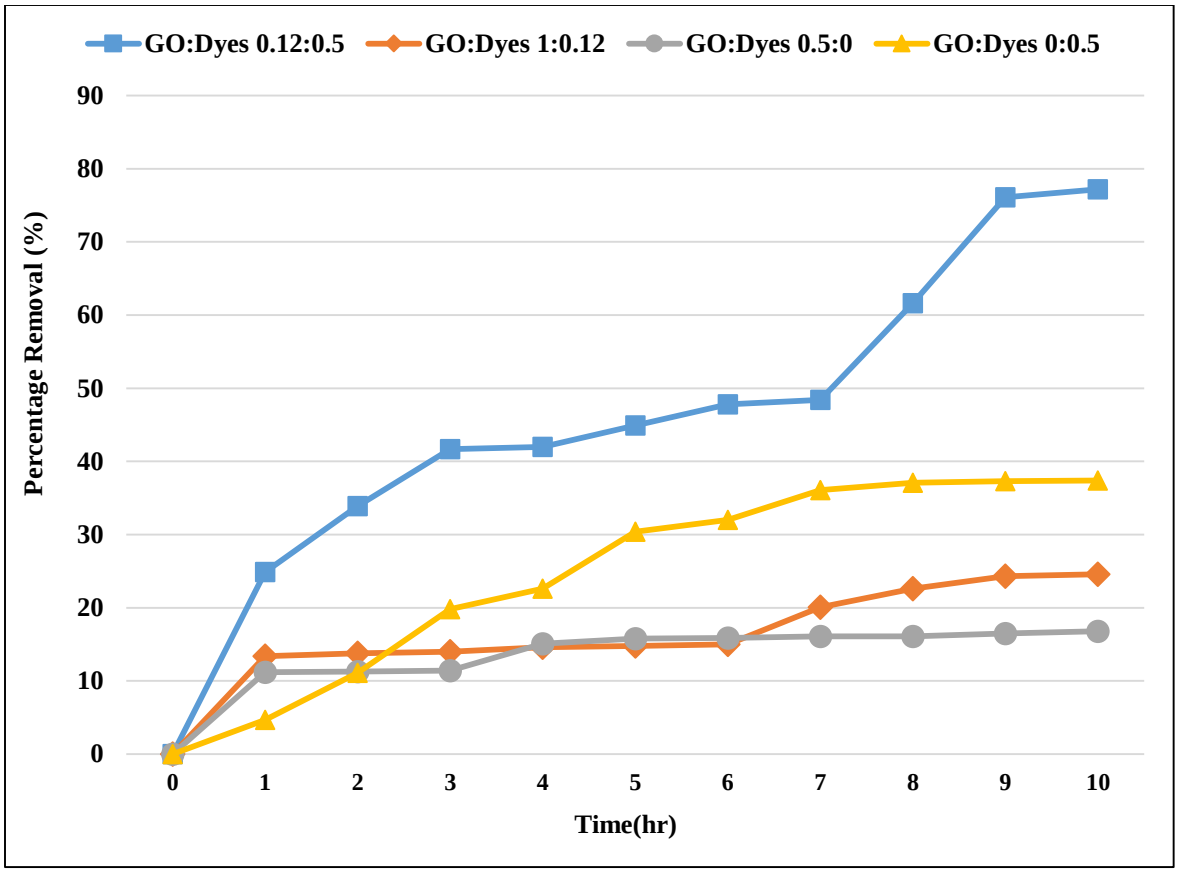


Figure 4.24: Effect of graphene oxide and dye dosage on phenol removal at pH 3 and 200 mg/L (200ppm) concentration

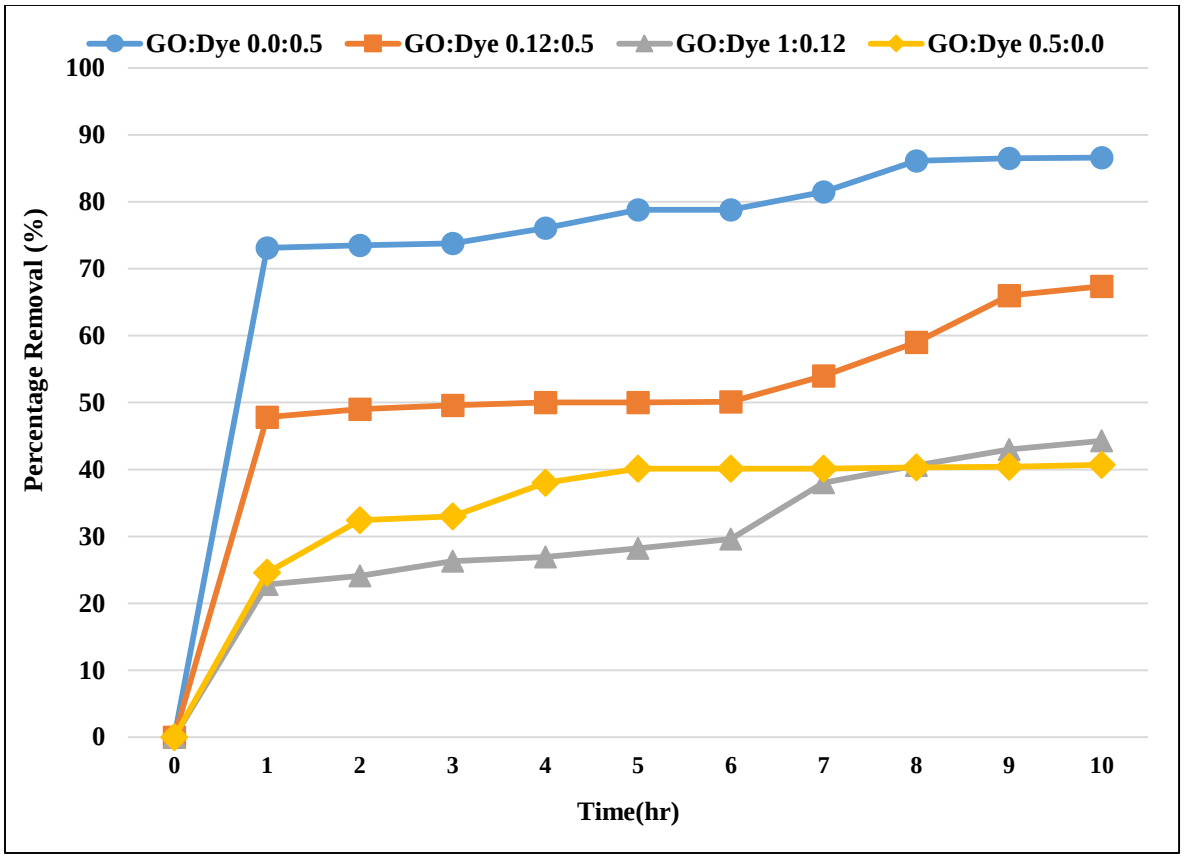


Figure 4.25: Effect of graphene oxide and dye dosage on phenol removal at pH 11 and 50 mg/L (50ppm) concentration.

4.3.4 Effects of Treatment Parameters on Phenol Removal

Several treatment parameters like pH, organic dye dosage, graphene oxide dosage, phenol concentration, contact time and efficiency of the flow reactor were examined to increase the phenol removal efficiency of the organic dye and the graphene oxide.

4.3.4.1 Effect of pH on Phenol removal

The effects of pH on the removal of phenol was assessed, pH 3 and pH 11 were used to determine the optimum removal pH. From (Figure 4.25 and Figure 4.26), there was prominent difference in phenol removal behavior under various pH conditions for both the graphene oxide and the organic dye where high removal was recorded at pH 11 the result is in line with reports of Maleki and Eslam which have report increase in pH increases removal of phenol (Maleki & Eslami, 2004). For both materials, 125 mL phenol spiked deionized water, stirred for 2 hour in a dark for adsorption and desorption equilibrium, 10 hours experiment time, with dosage of material ranging from 0-55mg and initial phenol concentration of 200 mg/L and 50mg/L were used in the pH study.

4.3.4.2 Effect of Time and the Phenol Concentration

Time taken to remove the phenol is another factor that was varied where time ranging from 1 hour to 10 hours was used because the time needed to reach optimum removal is dependent on the interaction time. In this study, we found that the more time given for the

material to interact with the phenol the better the removal. In some occasions time had no much effects particularly on the organic dye and graphene oxide alone at pH 3 with removal efficiency of 1% and 15% respectively however, in most cases the increase in time increased the removal capacity in both the graphene oxide and the organic dye and as the optimum condition was approached constant figure was recorded and this can be explained by the photocatalytic nature of the organic dye or the saturation point of the graphene oxide.

Effects of initial phenol concentration was also studied where 50mg/L and 200mg/L were used. The result showed that the percentage of phenol removal increases with increasing the organic dye and increasing the graphene oxide had no much effects on the phenol concentration however, the high removal of phenol was observed with increase of the photocatalyst organic dye rose bengal. This observation is in a good agreement with Gondal work which have reported increase in number of the exposed catalyst particles increases significant removal of phenol (Gondal, Sayeed, & Seddigi, 2008).

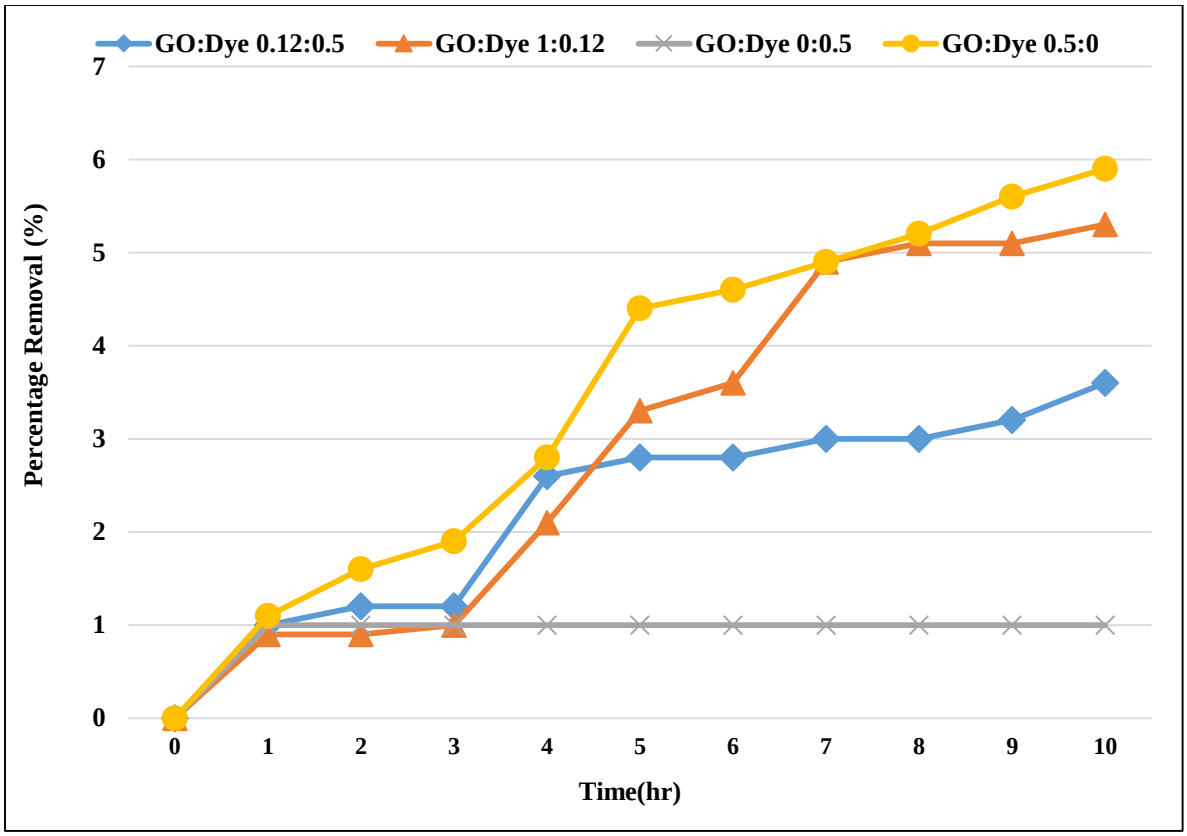


Figure 4.26: Effect of graphene oxide and dye dosage on phenol removal at pH 3 and 50 mg/L (50ppm) concentration.

4.3.4.3 Effect of Graphene oxide and organic dye on phenol removal

In order to determine and properly understand the effects of material dosage several experiments were performed. In this study the magnetic stirrer speed and the pump flow rate were fixed, phenol concentration was also either 50ppm or 200ppm, the pH was either 3 or 11 and the treatment time was ranging from 1 hour to 10hours.

From (Figure 4.25) it is clearly indicated that the organic dye has better removal capacity than the graphene oxide however, low removal potential at pH 3 was noted in both of the materials as shown in (Figure 4.26). Increase in the dosage of the graphene oxide had negative significance on the phenol removal while increase in the organic dye had positive significance on the removal despite of pH dependency as it's only effective at pH 11. Very low removal capacity of 1% was recorded at pH 3 for the organic dye however, increase in the organic dye increases the removal ability. The study result is in line with work done by Gondal which have reported increase in photocatalytic dosage increases phenol removal (Gondal et al., 2008). Increased graphene oxide dosage reduced the efficiency of the removal which can possibly be correlated to the overlapping behavior of adsorption sites resulting in reduction in the surface area available for the phenol adsorption or the effect of the flow reactor setup. The result is similar to work done by Moyo and his team. (Moyo et al., 2012)

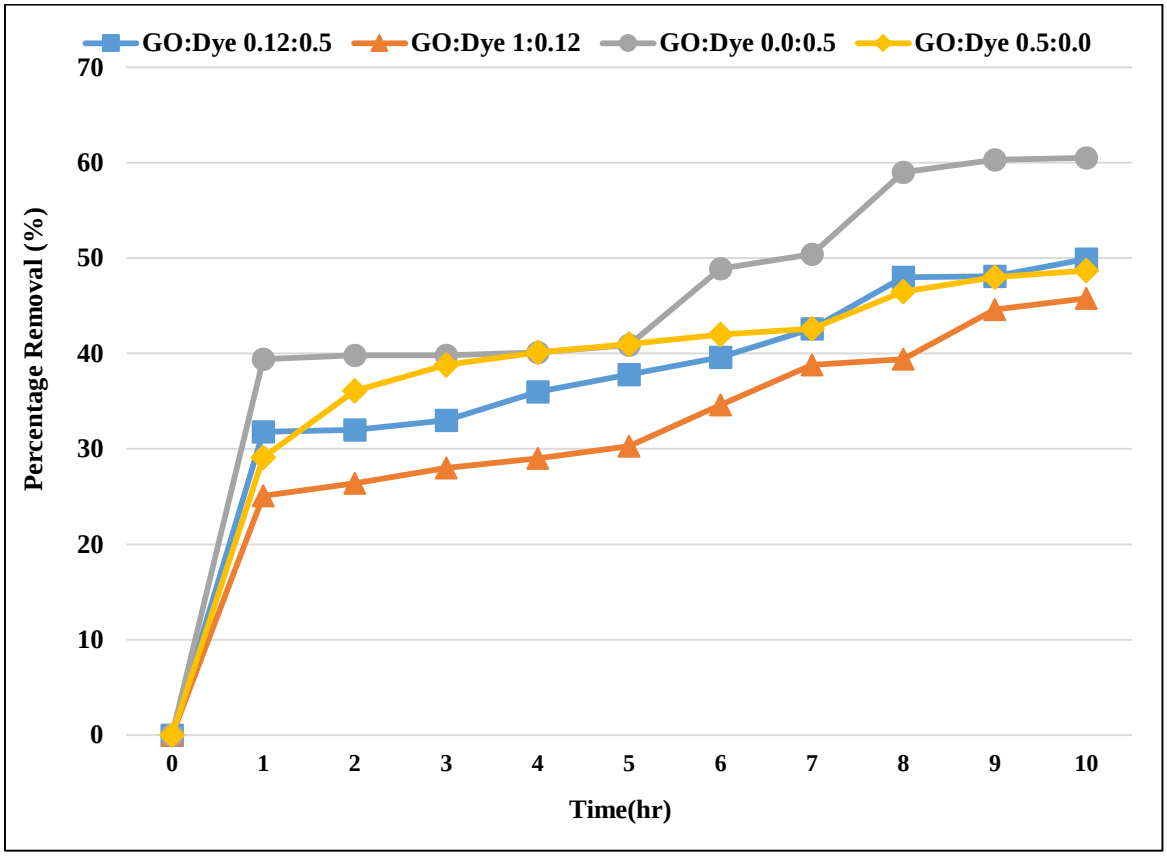


Figure 4.27: Effect of graphene oxide and dye dosage on phenol removal at pH 11 and 200 mg/L (200ppm) concentration

4.3.4.4 Effect of continuous flow reactor on the removal of phenol

The effect of flow rector was also investigated in this study at different pH, dosage, phenol concentration and the result compared with a vial that was subjected to the direct sunlight without the flow reactor for 10 hours as shown on (Figure 4.28 to Figure 4.31). At pH3 and phenol 200 mg/L (200ppm) concentration we have recorded 39% improvement in the treatment process with a flow reactor, at pH 3 and 50 mg/L (50ppm) concentration 22.1% improvement was noted, at pH 11 and 200 mg/L (200ppm) concentration 11.7% improvement was observed and least improvement was noted at pH 11 and 50 mg/L (50ppm) concentration with 9.6%. In general the designed continuous flow reactor has enhanced the treatment process and the degradation of the phenol by 20.6% and the finding is in consistent with study done by Pulgarin and his group who have reported solar reactor treatment of bio recalcitrant pollutants which showed same trend (Sarria, Kenfack, Guillod, & Pulgarin, 2003).

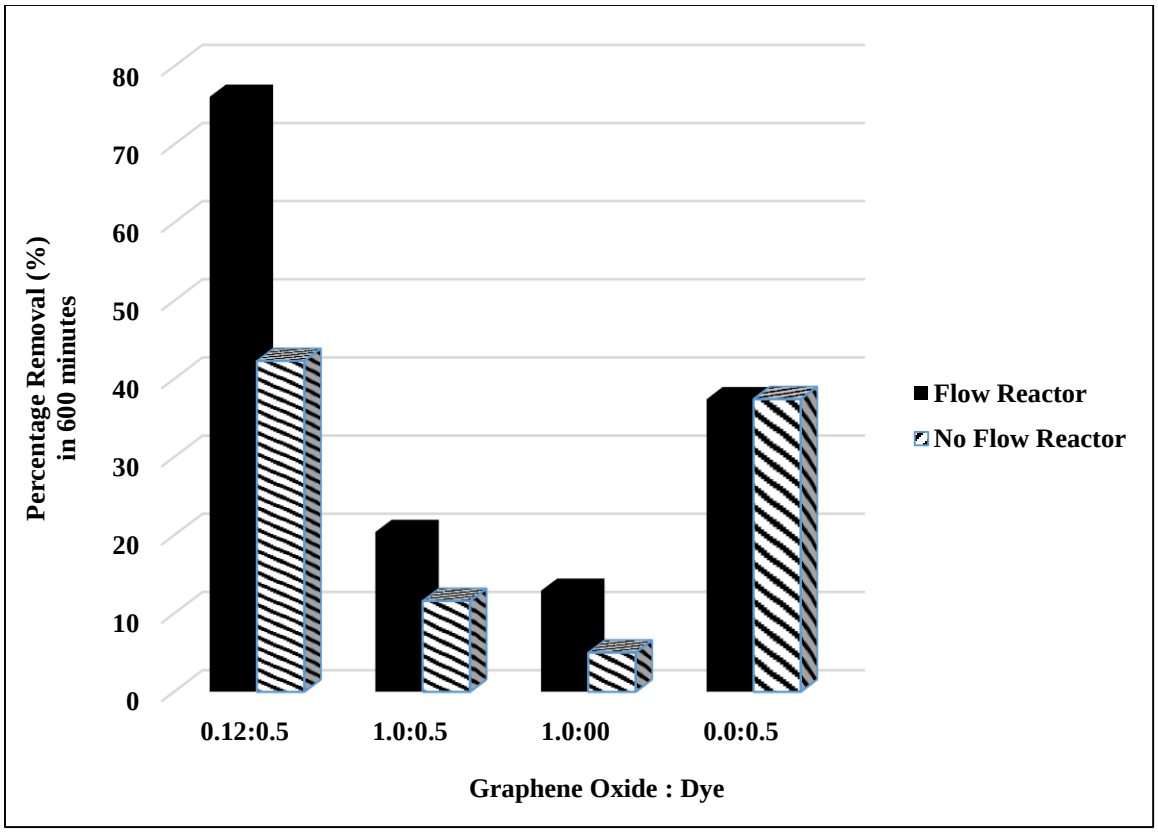


Figure 4.28: Effect of flow reactor on phenol removal at pH3 and 200 mg/L (200ppm) concentration

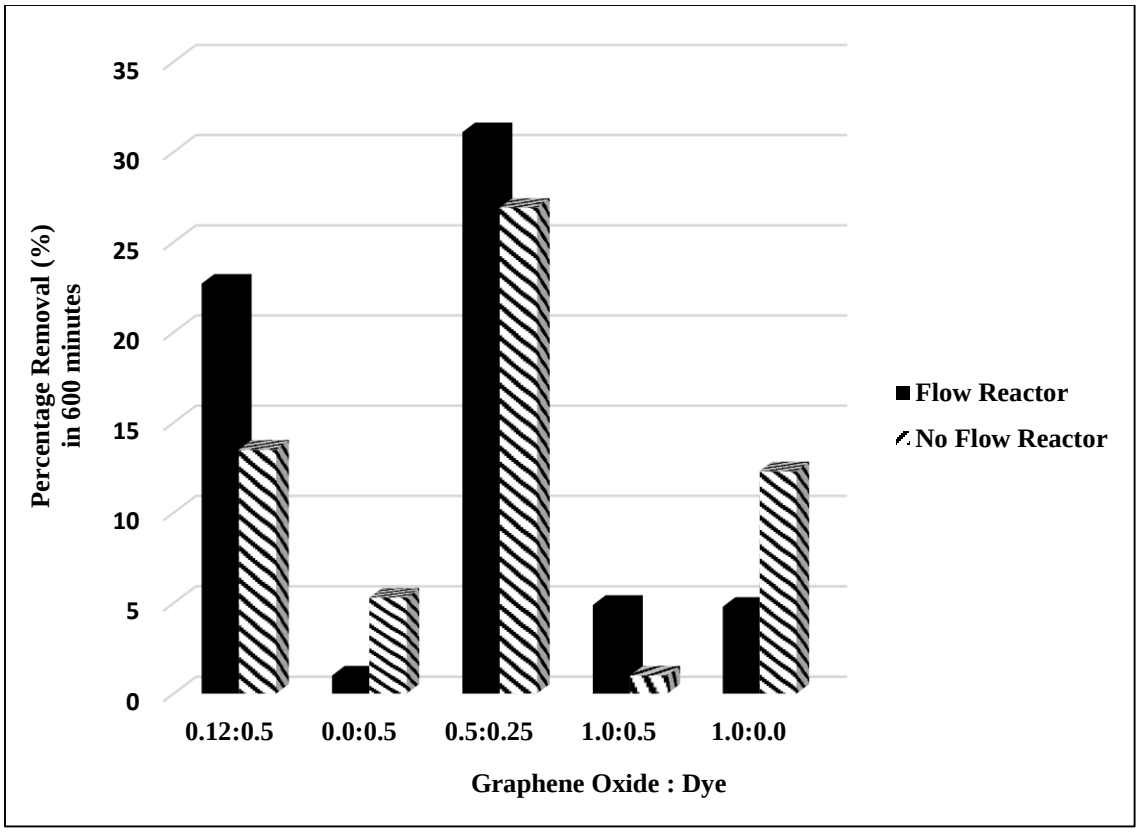


Figure 4.29: Effect flow reactor on phenol removal at pH 3 and 50 mg/L (50ppm) concentration

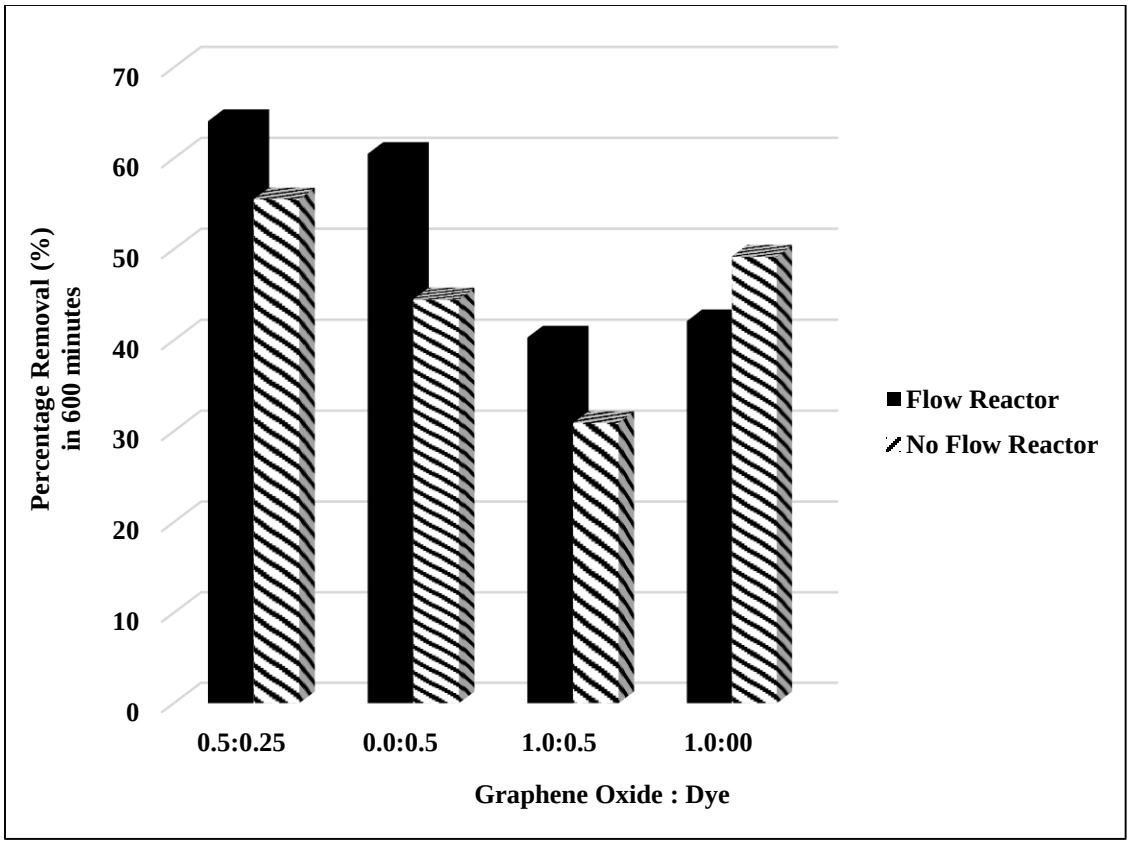


Figure 4.30: Effect of flow reactor on phenol removal at pH 11 and 200 mg/L (200ppm) concentration

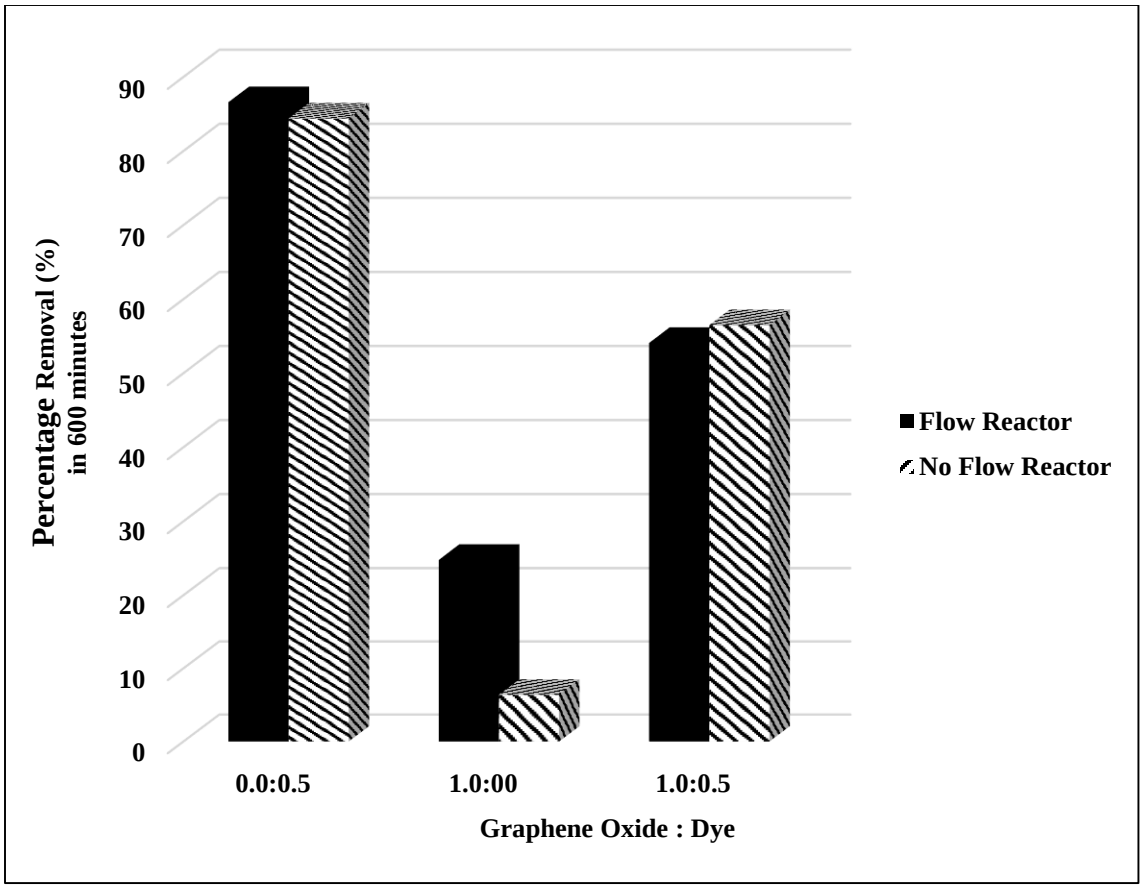


Figure 4.31: Effect of flow reactor on phenol removal at pH 11 and 50 mg/L (50ppm) concentration.

4.3.5 Optimization Conditions for the Removal of Phenol

The study has used Minitab statistical data for the optimization of the experiments. Since we have just seen the comparison of different effects such as main effects plot for percentage removal, interaction plot for percentage removal, Pareto chart of the standardized effects and also normal plot of the standardized effects were plotted as shown on Figure 4.32 to Figure 4.31 and the experimental results were analyzed. In this study, ANOVA design was performed to confirm whether the phenol removal was really effective by different kinds of treatment parameters or not. Minitab was used for ANOVA and constructing plots. As can be concluded from the results of ANOVA the pH parameter and organic dye dosage are more significant than all the other parameters.

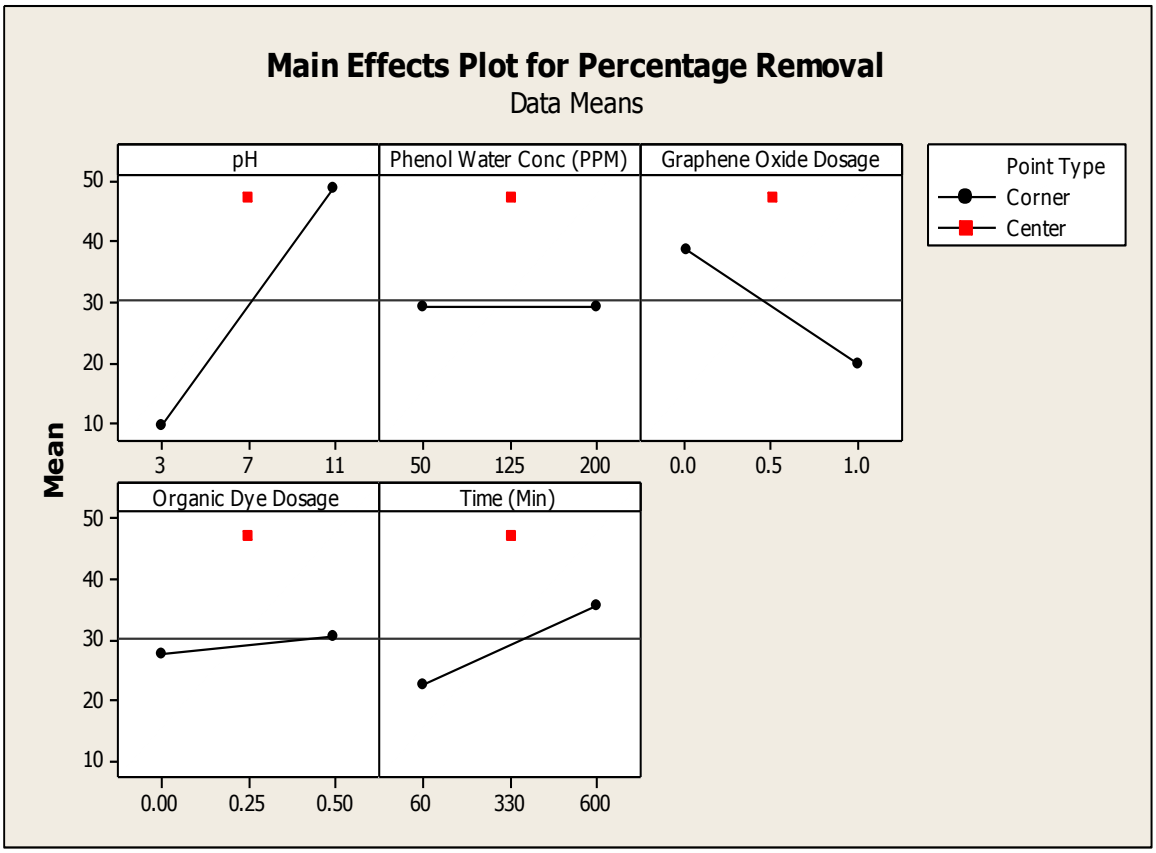


Figure 4.32: Main Effects plot for percentage removal

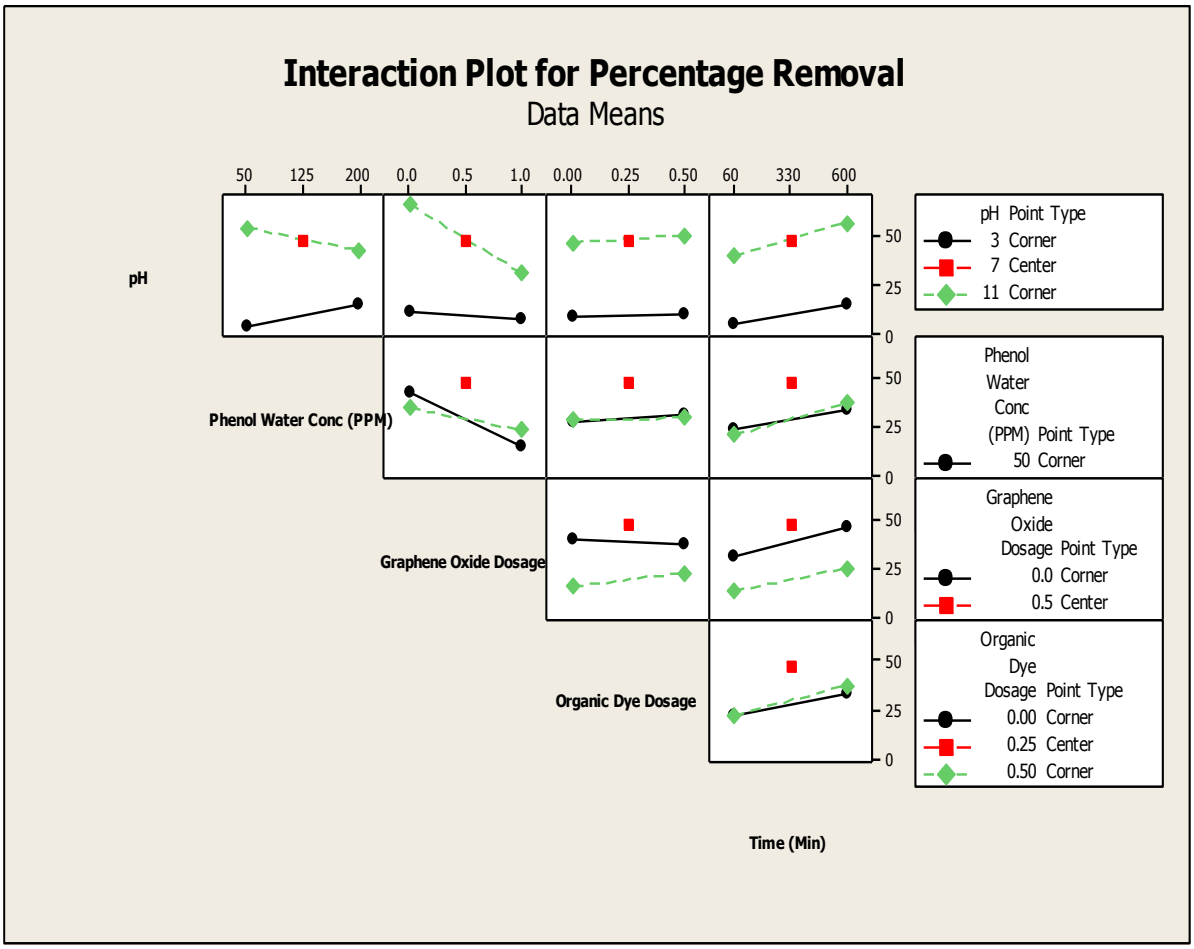


Figure 4.33: Interaction Plot for Percentage Removal

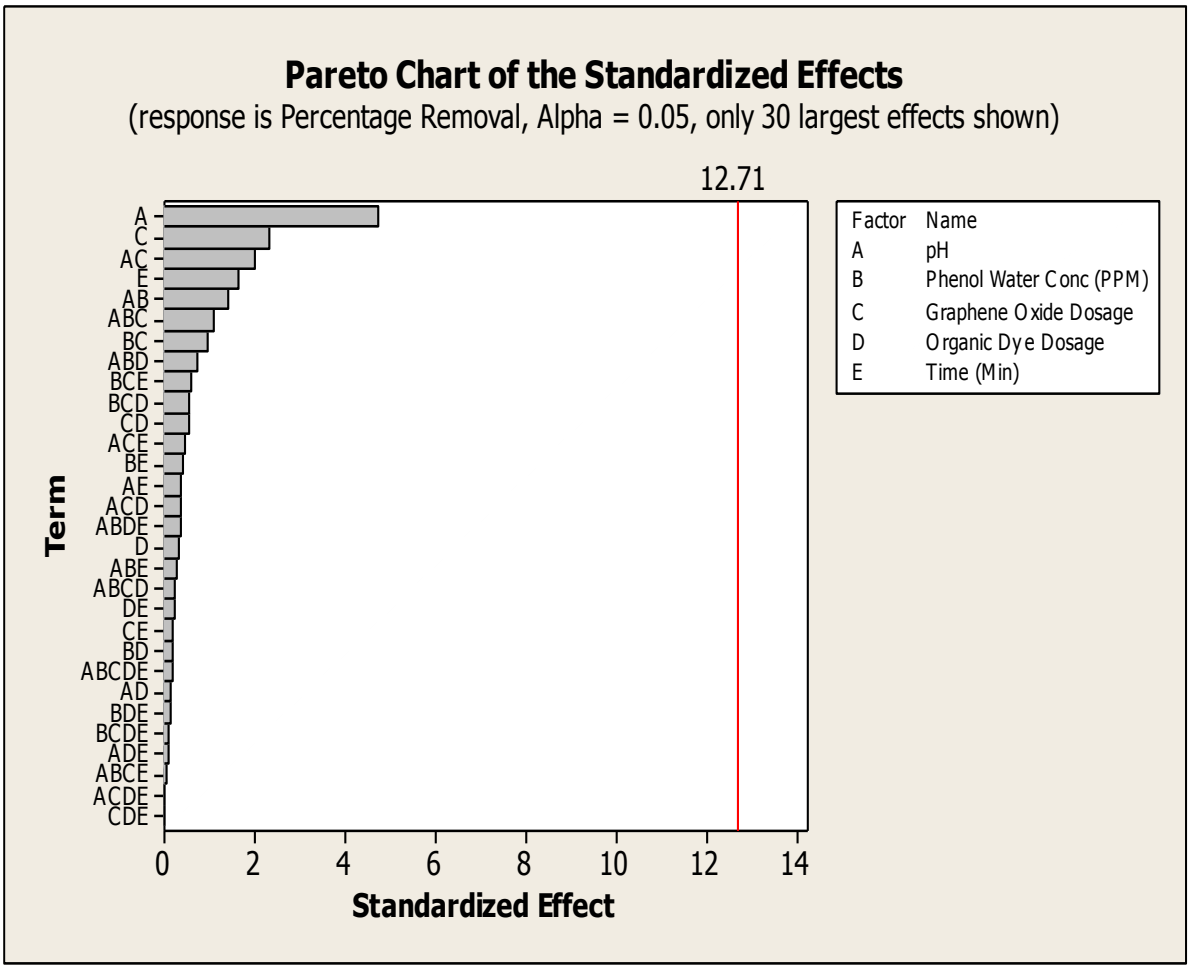


Figure 4.34: Pareto Chart of the Standardized Effects

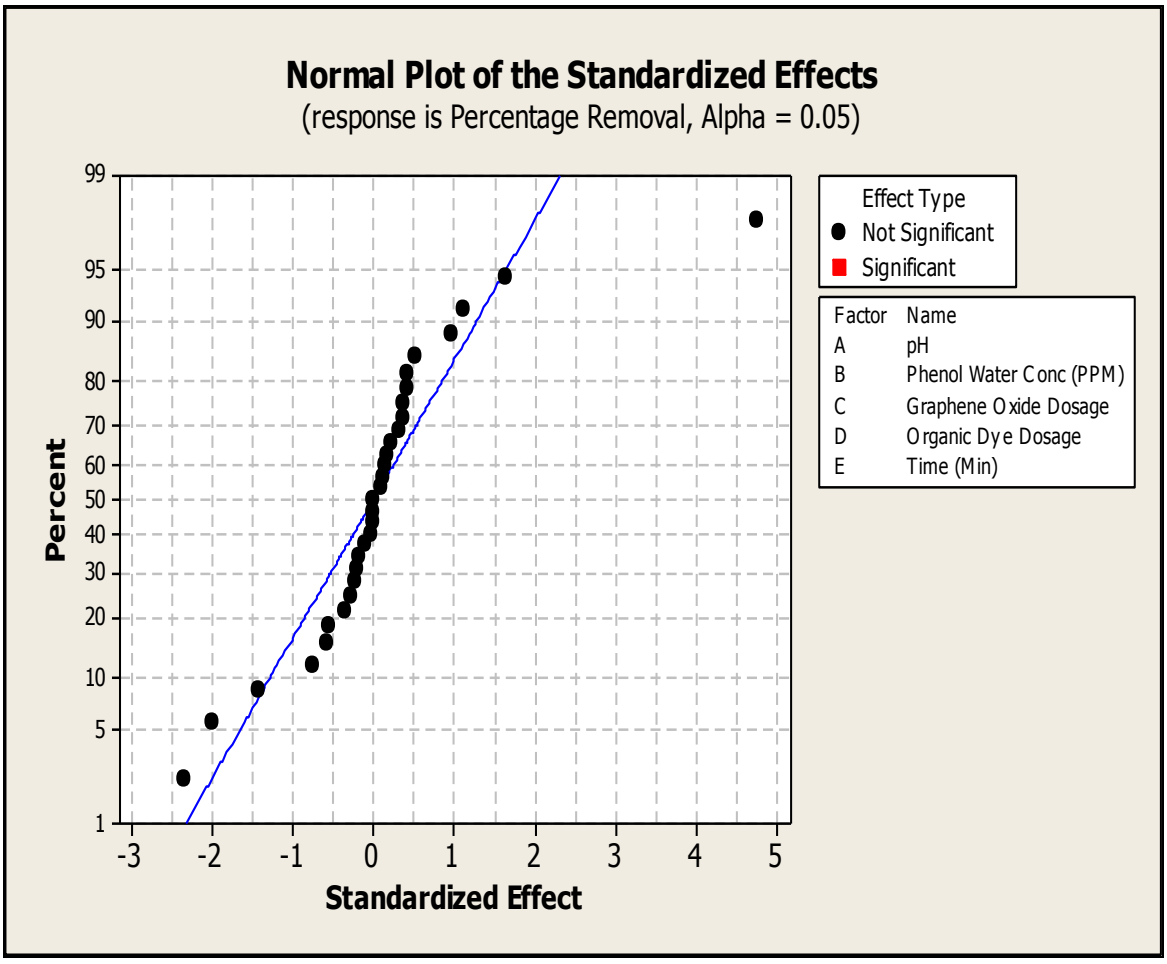


Figure 4.35: Normal Plot of the Standardized Effects

4.3.6 Optimized Conditions for the Phenol Removal

The observations drawn from this study indicate that optimum phenol removal from water was achieved when only organic dye rose bengal was used with removal efficiency of 86.6%. The pH of the water was found to be influencing the phenol removal with peak attained at pH 11. The optimum dosage was 27.5mg of the organic dye rose bengal. Also the adsorption equilibrium was observed after 7 hours treatment time. The mechanism of phenol removal in this study was exclusively attributed to its photocatalytic role of the organic dye, as the presence of only the graphene oxide has shown no much phenol removal but enhanced treatment was attained when the dye dosage is increased and the graphene oxide reduced as removal condition recorded under this study conditions. The optimum condition graph is shown on (Figure 4.36)

Therefore in this study the photo-catalytic breakdown of phenol is the hydroxylation of the phenyl ring in water. The likely expected process of photo-reduction of phenol within the water is based upon the formation of hydroxyl radical ($^{\bullet}HO$) and H+ ions through water oxidation by the valence band holes produced due to sunlight irradiation having photon energy ($h\nu$) $\geq$ band gap of a semiconductor catalyst rose bengal organic dye in water. The hydroxyl radicals produces oxygen while H+ ions form hydrogen by taking conduction band electrons in a de-oxygenation solution. The production of hydrogen and oxygen by water splitting using catalyst was demonstrated by Gondal and his team (Gondal et al., 2008). The •HO and oxygen generated through the photo-catalytic process are responsible for reduction of phenol. The •HO produced by water splitting breaks the phenol into CO_2 and water.

$$\textbf{Rose Bengal} \xrightarrow{h\upsilon > E_g} \textbf{Rose Bengal}\ (h_{vb}^{+} + e_{cb}^{-})$$

$$H_2O + h_{vb}^{+} \rightarrow\ H_2O^{+} \rightarrow OH^{\bullet} +\ H^{+}$$

$$C_6H_6O + 12OH^{\bullet} \rightarrow 6CO_2 + 9H_2O$$

$$C_6H_6O + 7O_2 \rightarrow 6CO_2 + 3H_2O$$

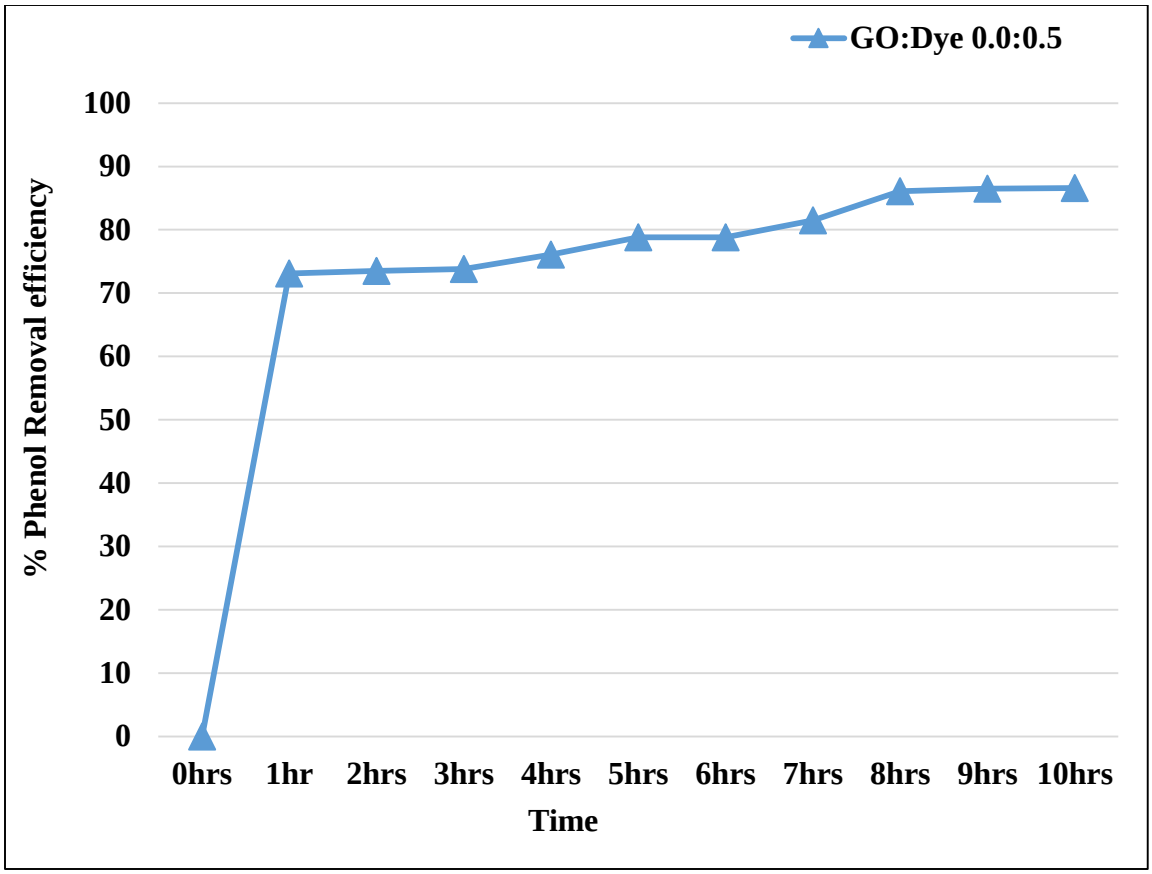


Figure 4.36: Percentage Phenol removal from contaminated water with organic dye Rose Bengal alone compared with graphene oxide alone at the same dosage, at pH 11 and 50 mg/L phenol concentration.

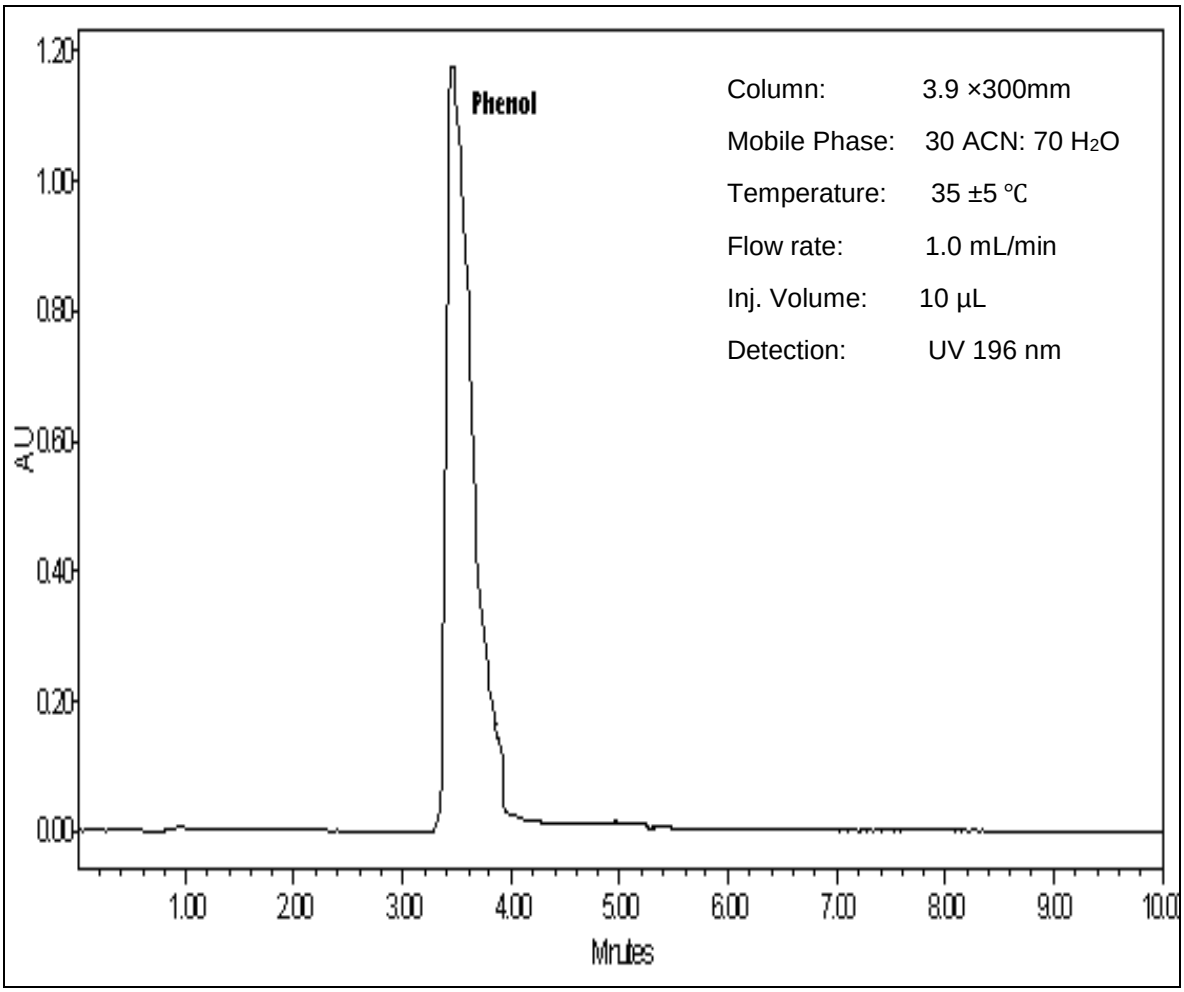


Figure 4.37: HPLC chromatogram showing 200 mg/l (200PPM) phenol concentration at pH 11 before the treatment with graphene oxide: organic dye 0:0.5 dosage.

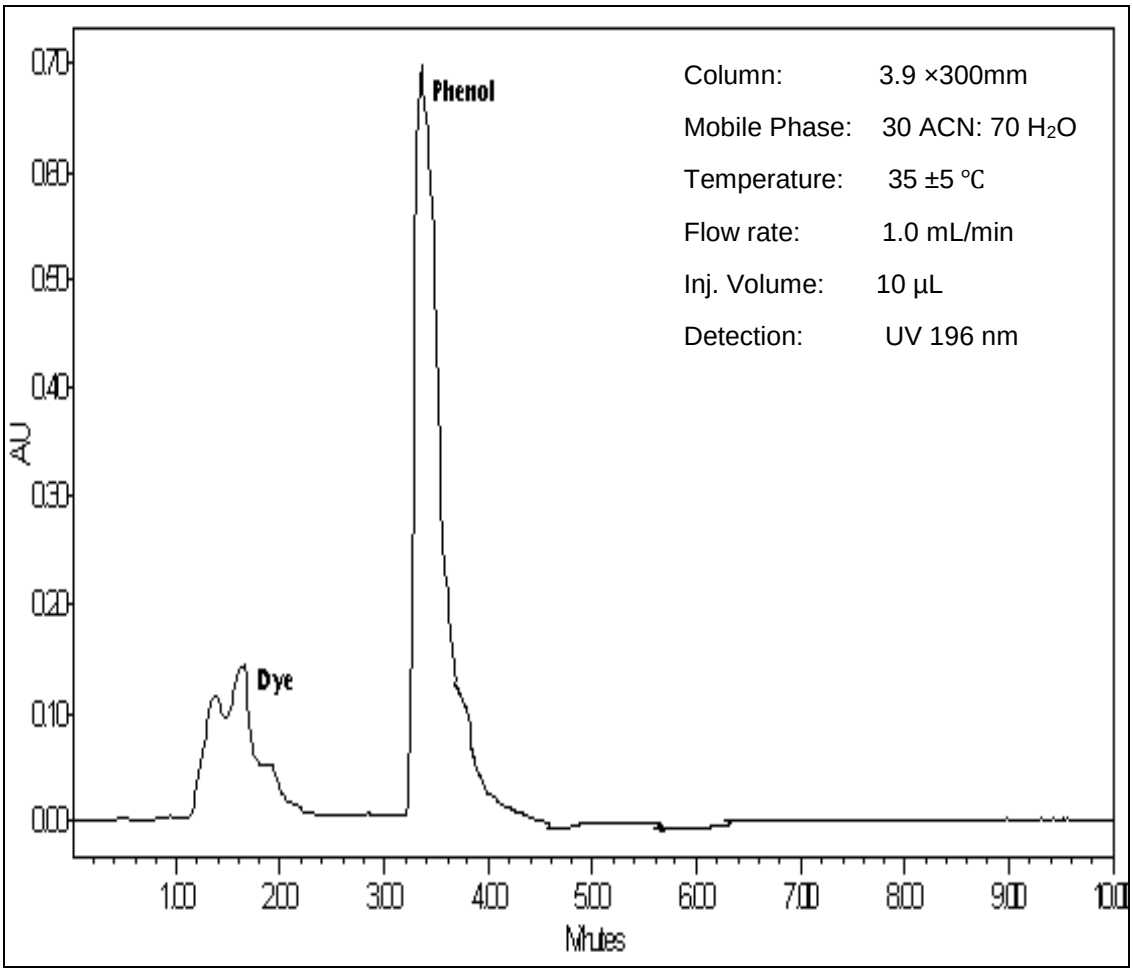


Figure 4.38: HPLC chromatogram showing 200 mg/l (200PPM) phenol concentration at pH 11 after 1 hour treatment with graphene oxide: organic dye 0:0.5 dosage.

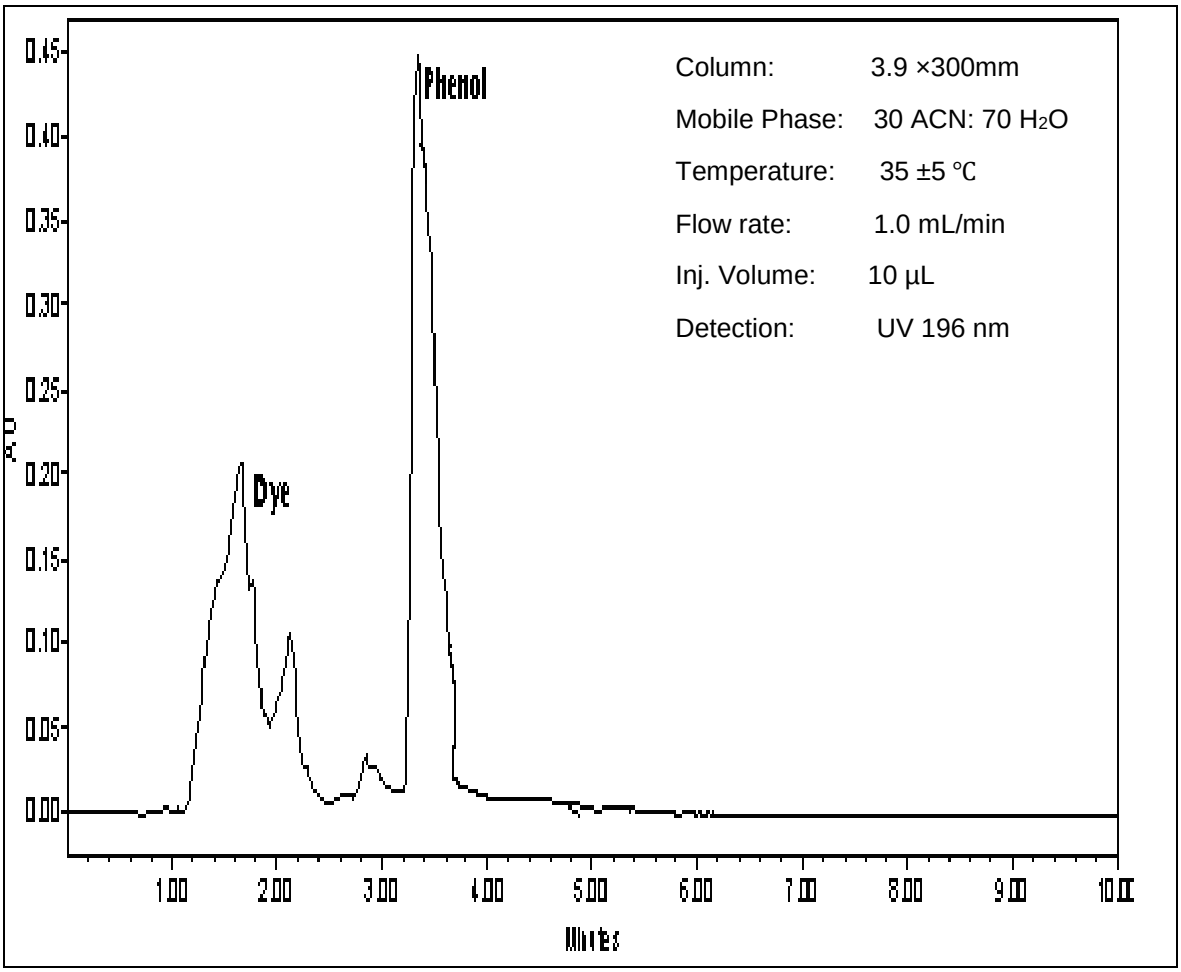


Figure 4.39: HPLC chromatogram showing 200 mg/l (200PPM) phenol concentration at pH 11 after 10 hour's treatment with graphene oxide: organic dye 0:0.5 dosage.

.

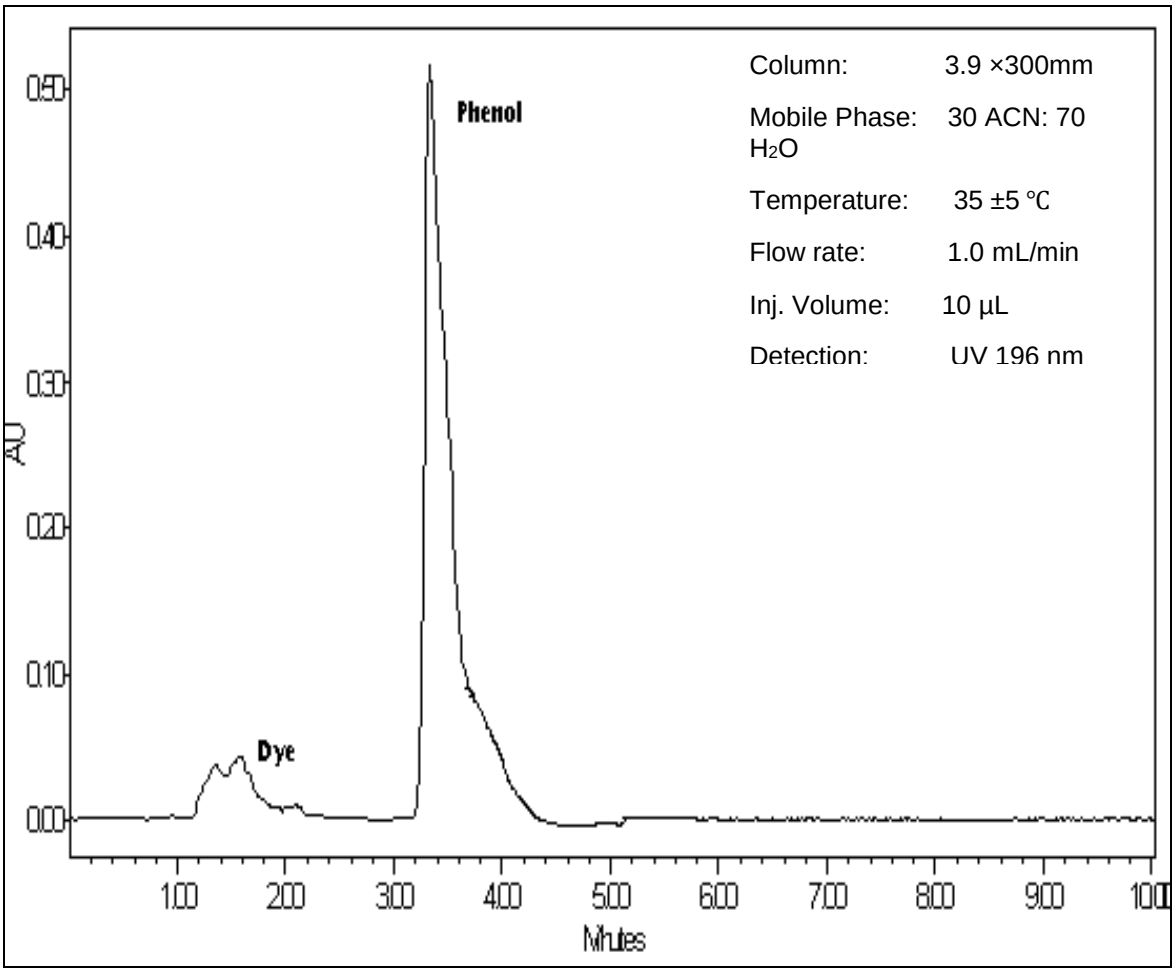


Figure 4.40: HPLC chromatogram showing 200 mg/l (200PPM) phenol concentration at pH 11 after 10 hour's treatment without flow reactor with graphene oxide: organic dye 0:0.5 dosage.

.

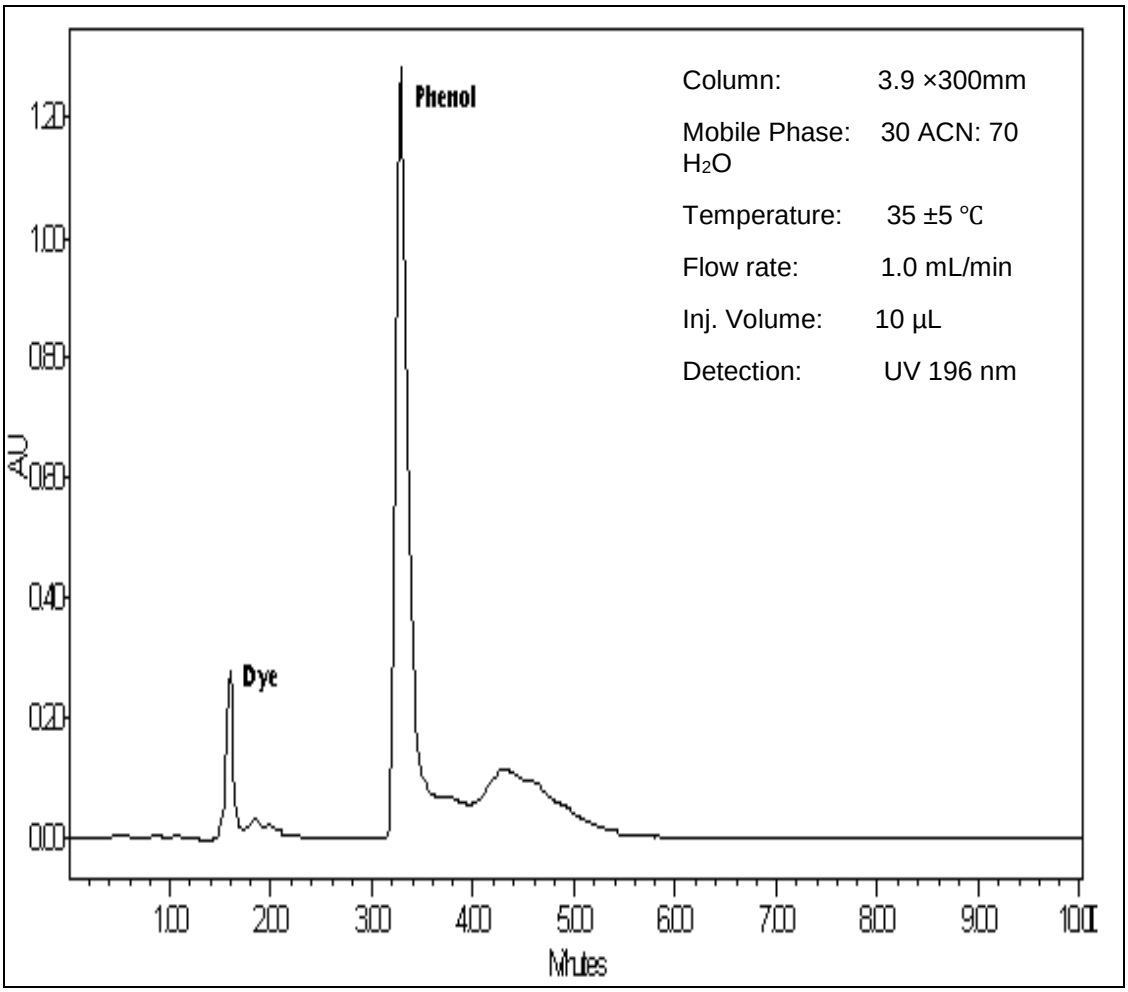


Figure 4.41: HPLC chromatogram showing 200 mg/l (200PPM) phenol concentration at pH 3 before the treatment with graphene oxide: organic dye 0.12:0.5 dosage.

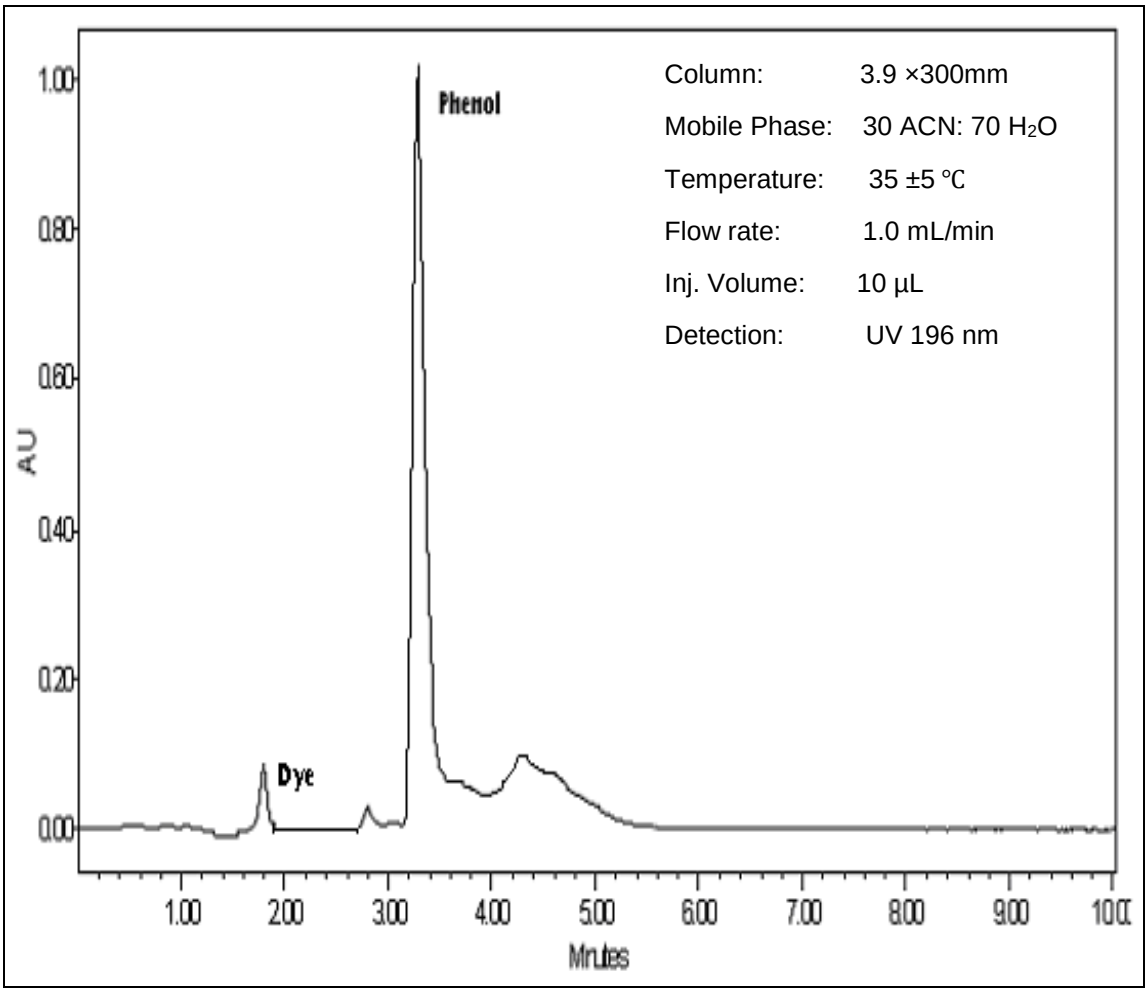


Figure 4.42: HPLC chromatogram showing 200 mg/l (200PPM) phenol concentration at pH 3 after 1 hour treatment with graphene oxide: organic dye 0.12:0.5 dosage.

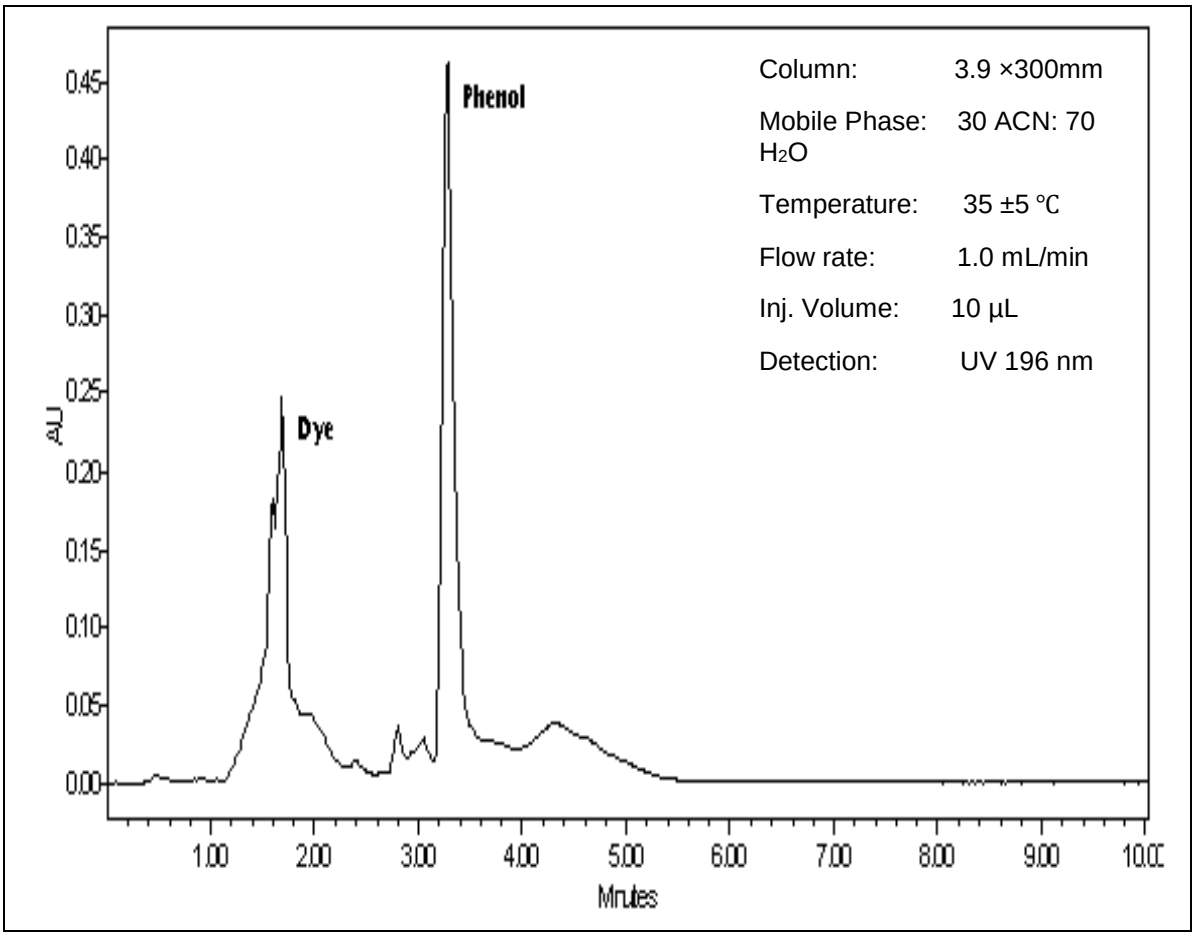


Figure 4.43: HPLC chromatogram showing 200 mg/l (200PPM) phenol concentration at pH 3 after 10hours treatment with graphene oxide: organic dye 0.12:0.5 dosage.

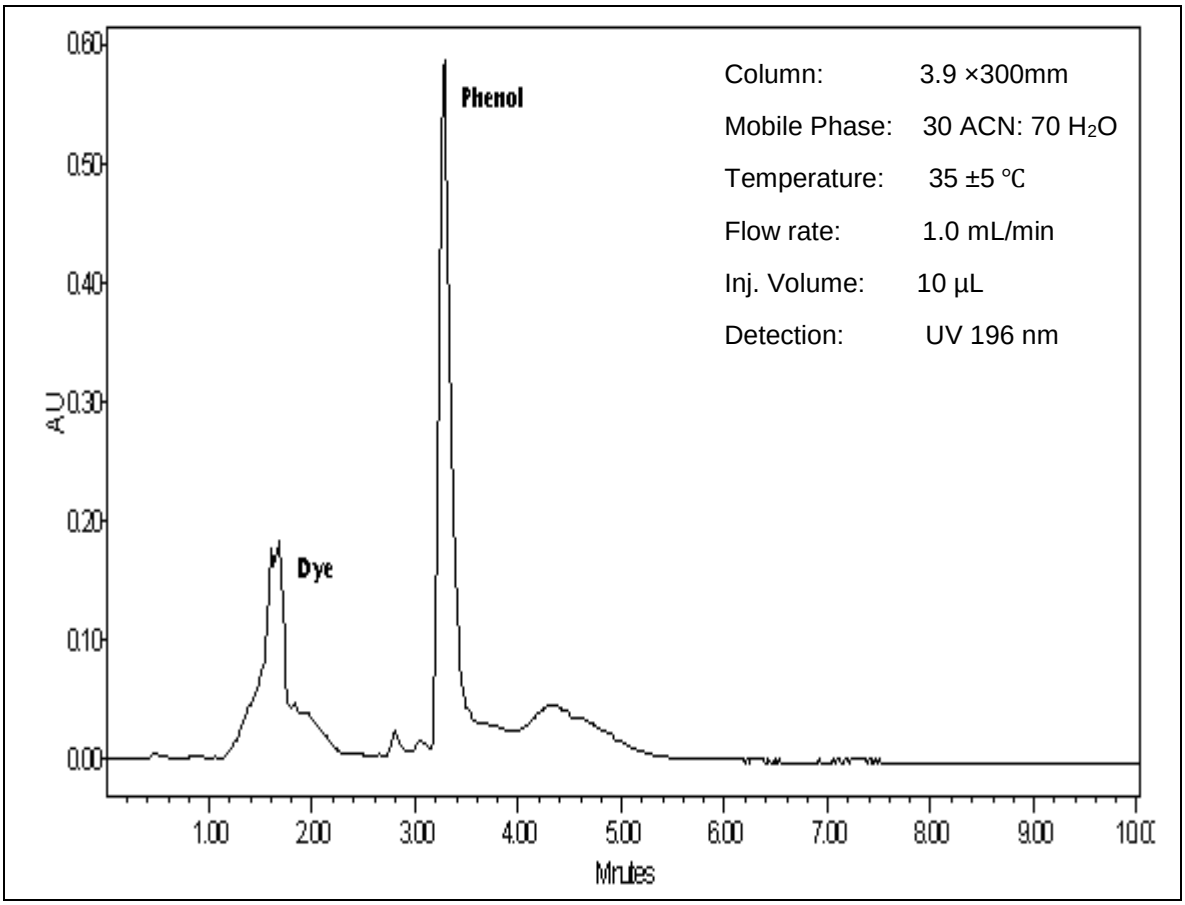


Figure 4.44: HPLC chromatogram showing 200 mg/l (200PPM) phenol concentration at pH 3 without flow reactor with graphene oxide: organic dye 0.12:0.5 dosage.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The main objective of this study was to assess the ability of natural sunlight and environmental friendly organic dyes in organic synthesis and degradation of phenol in water through a designed continuous capillary flow reactor. The aim generally was to understand how various experimental variables and the flow reactor had an influence on the reaction, the treatment process and set an optimum conditions under which the best possible yield and removal of phenol from water can be achieved.

Following the evidences from literature, natural sunlight has successfully been used in both contaminants degradation and organic synthesis, also organic dyes have been reported to be excellent photocatalysts and furthermore, flow reactors in many studies was proved to enhance yield. The motivations behind this study was solely based on the achievements reported in other studies in both the synthesis and the treatment process.

Optimization of the experiments were carried out to establish an optimized green procedure for both the α-Functionalization of tertiary amines and α-oxyamination of 1,3-dicarbonyl compounds. Optimization of reaction solvent was carried out using water, acetonitrile and dichloromethane with 84%, 93% and 33.5% yield respectively. Water showed a green alternative to both acetonitrile dichloromethane in α-oxyamination reactions.

A detailed study was done on the photosensitizers that demonstrated high yield in the use of rose bengal organic dye compared to fluorescein and eosin Y. For future applications, recycling and reuse of the light sensitizers can be optimized, as well as a detailed more study of optimum concentration and mixing of the sensitizer in the reaction solution can be extended.

The use of the continuous flow reactor was also investigated in each experiment to optimize reactor efficiency. The flow reactors provided various advantages for photochemical synthesis. When the optimized conditions were applied an average improvement of 26.4% in α-oxyamination and 60.8% in α-Functionalization of tertiary amines were noted with the use of continuous flow reactor. High yield recorded in α-Functionalization of tertiary amines with use of flow reactor can be attributed to the maximum contact between reaction solution and oxygen, as oxygen is essential for the reaction. Manipulation of flow rate and residence time could also increase the conversion achieved, as this study was limited by the minimum capacity of the pump used. Solvent-free synthesis was suitable and successful for α-Functionalization of tertiary amines reaction because Nitromethane was used as solvent and reactant at the same time.

The results obtained from this study showed that the graphene oxide alone was unable to obtain significant phenol removal in water, as low as 4.8% removal was noted however, at pH 11 on the same condition and dosage of the graphene oxide 42% reduction of phenol was recorded. In contrary the organic dye only at pH 11 and 50ppm phenol concentration has shown excellent phenol removal of 86.6% where efficiency was obtained. The effects of different experimental variables like pH was also assessed in this study, with both organic dye and graphene oxide showing positive response with increase in pH. Having

recorded higher percentage removal of phenol by organic dye Rose Bengal alone, more experiments were conducted on this material, and the excellent removal condition needed was established to be 50mg/L phenol concentration in water, pH 11 and maximum time of 10 hours.

Additional work was done to establish the effects of the combination of the graphene oxide and the organic dye and the result was not promising as it dropped from 86.6% to 54.1% with increase in graphene oxide which can be probably masking the role of the organic dye however, successful removal was observed with increase in organic dye dosage. Furthermore, the effect of the designed flow reactor on the removal of phenol was also investigated and the finding was an average improvement of 20.6% phenol degradation with the use of flow reactor compared to the results without flow reactor.

This reflection of the result lead to the conclusion that photocatalytic material like organic dye rose bengal only can be used to remove phenol from water and graphene oxide lowering the efficiency of the organic dye hence decline in removal ability. The capacity of organic dye Rose Bengal for the degradation of phenol is presented here that showed high removal efficiency of nearly 87%.

5.2 Recommendations

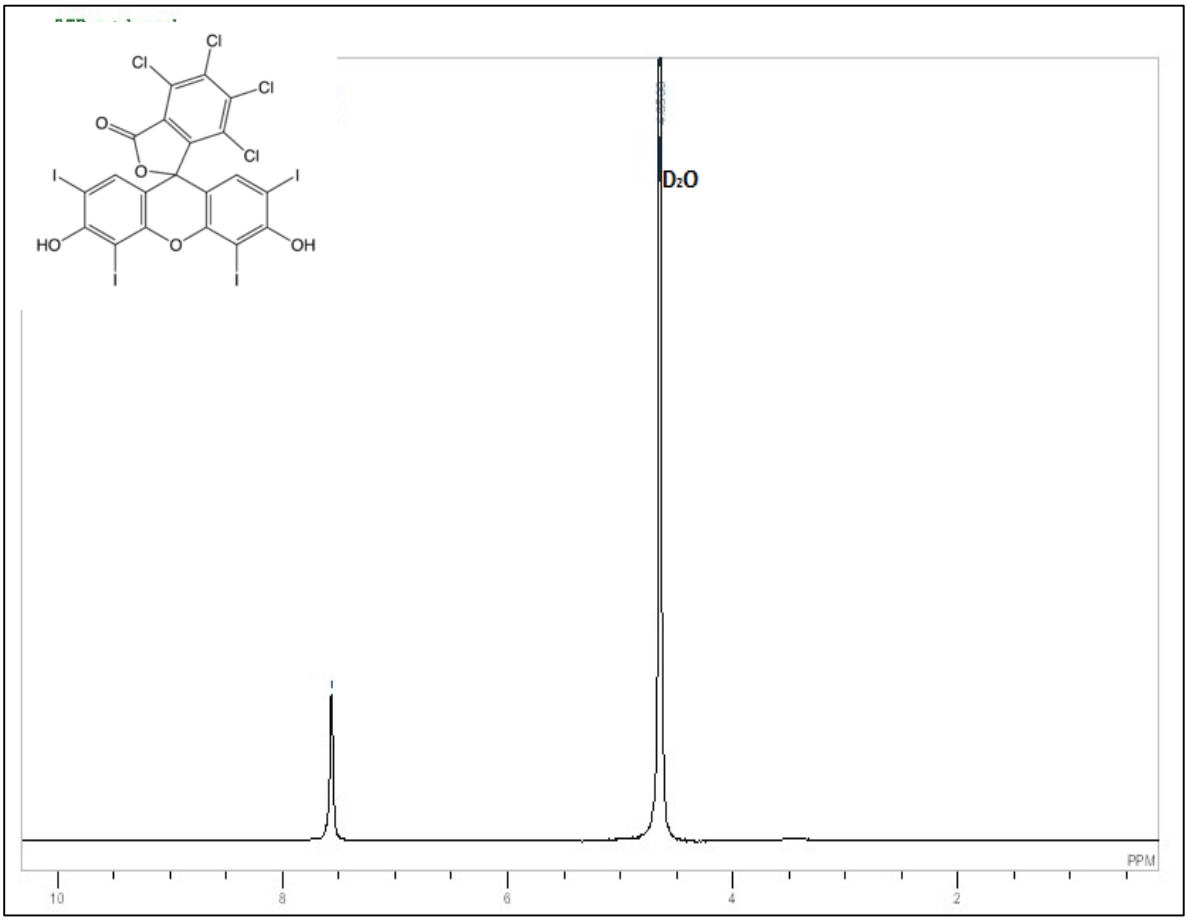
From this study following recommendations are made to contribute and advance the scientific knowledge on this work;

1. Future research works should look at the optimization of synthesis, as well as recovery, reuse and recycling of the organic dyes photocatalyzed reactions.

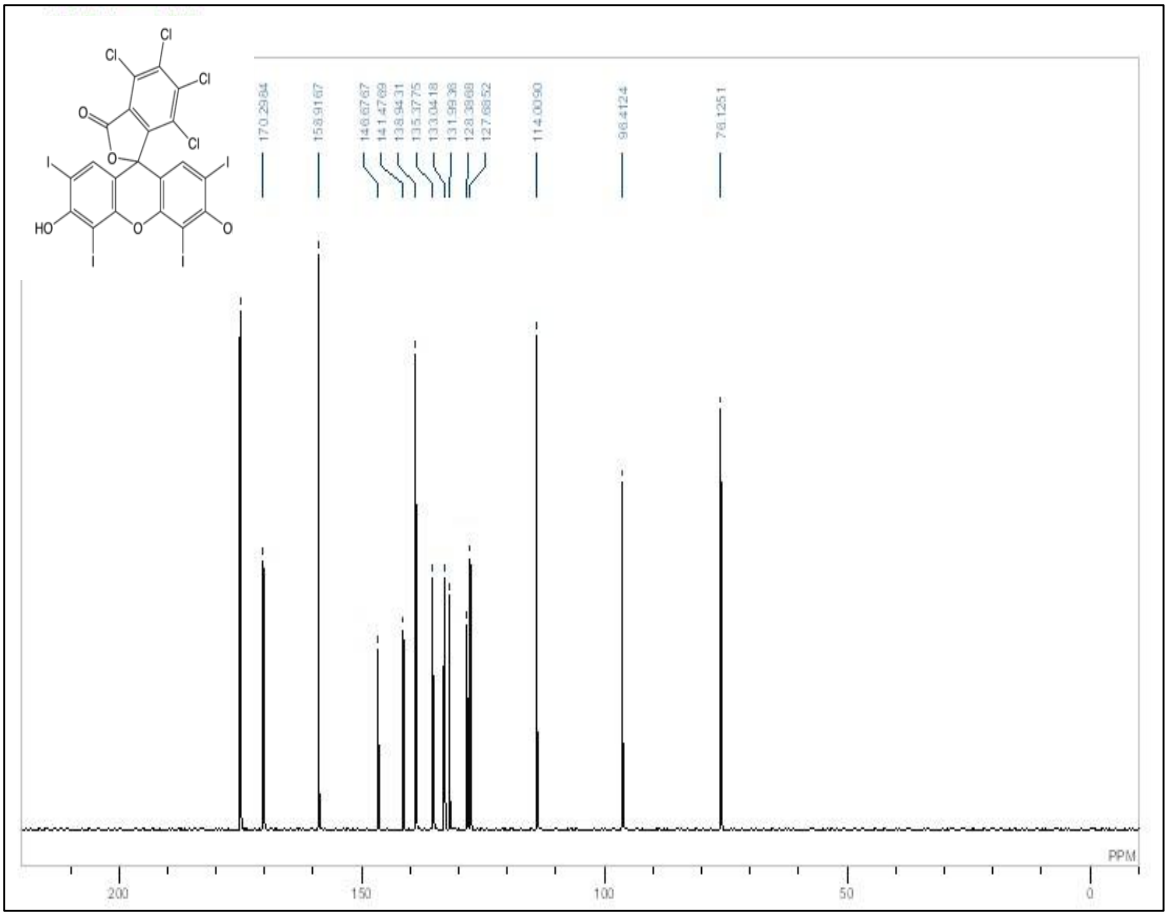
2. Improvement and scale up of the continuous flow reactor with wavelength adjustment knob to suit sensitizer absorption region is a possibility.
3. More studies on various organic dyes to remove phenol and other organic pollutants can be investigated.
4. Combine different organic dyes to investigate the synthesis and removal efficiency of phenol and other pollutants
5. Successive more research work can be initiated by combining organic dyes with other adsorbents like reduced graphene oxide and silver nanoparticles to understand removal capacity of phenol and other pollutants.
6. Application of flow reactor, organic dyes and natural sunlight can be extended to the treatment of other environmental pollutants.
7. The treatment of phenol using organic dyes in the presence of sunlight through a flow reactor requires more research work like kinetics to understand it better.

APPENDICES

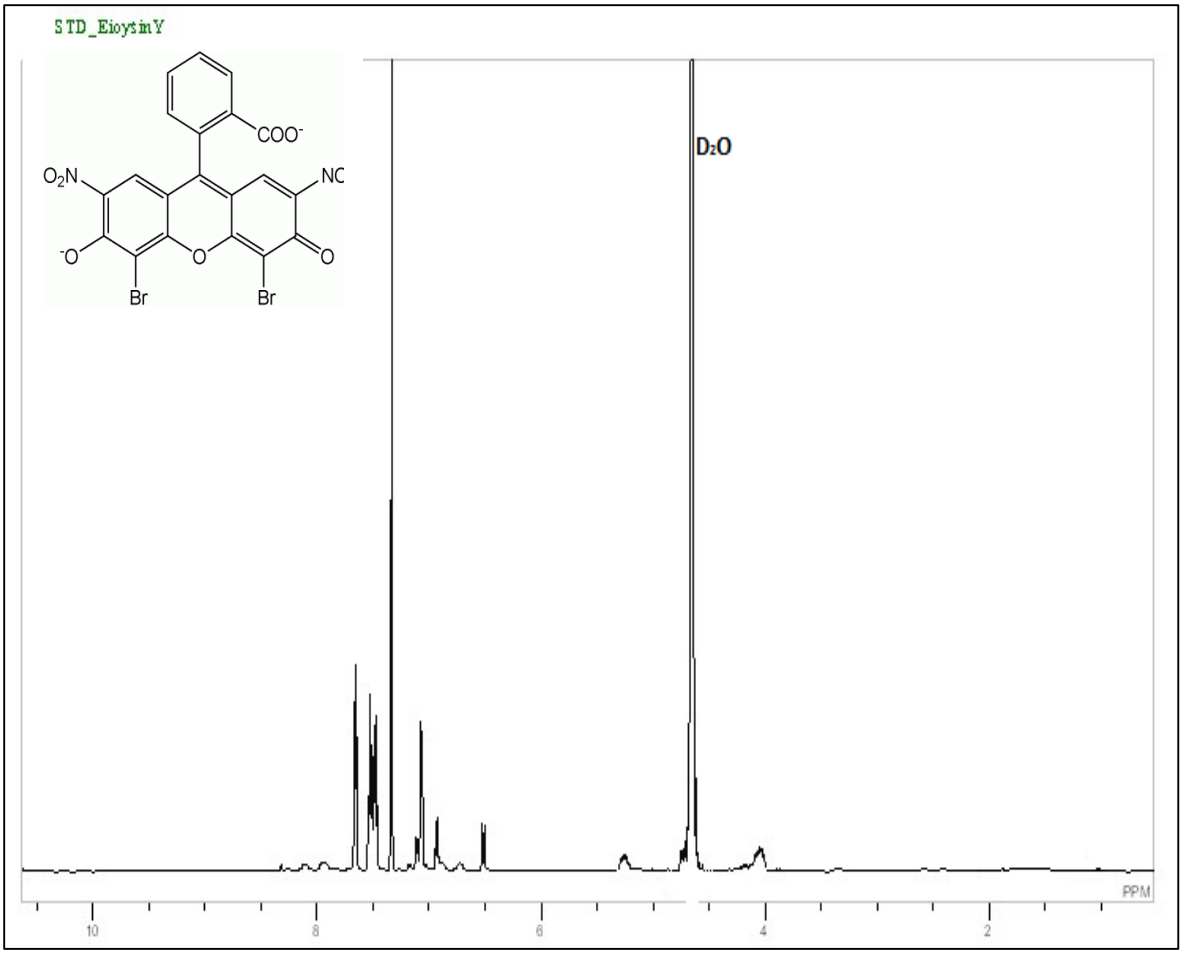
APPENDIX A: NMR OF STARTING MATERIALS



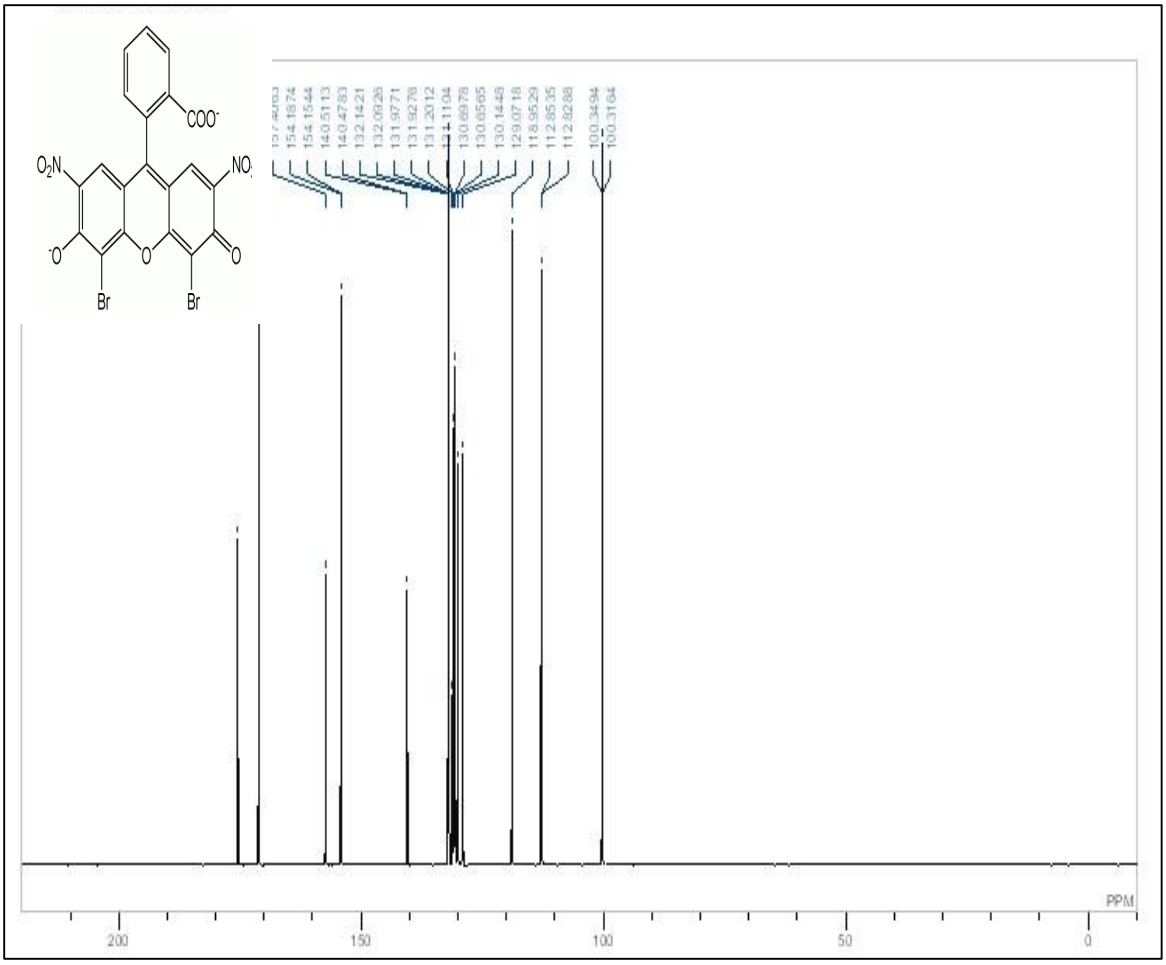
[1]HNMR of Rose Bengal dye.



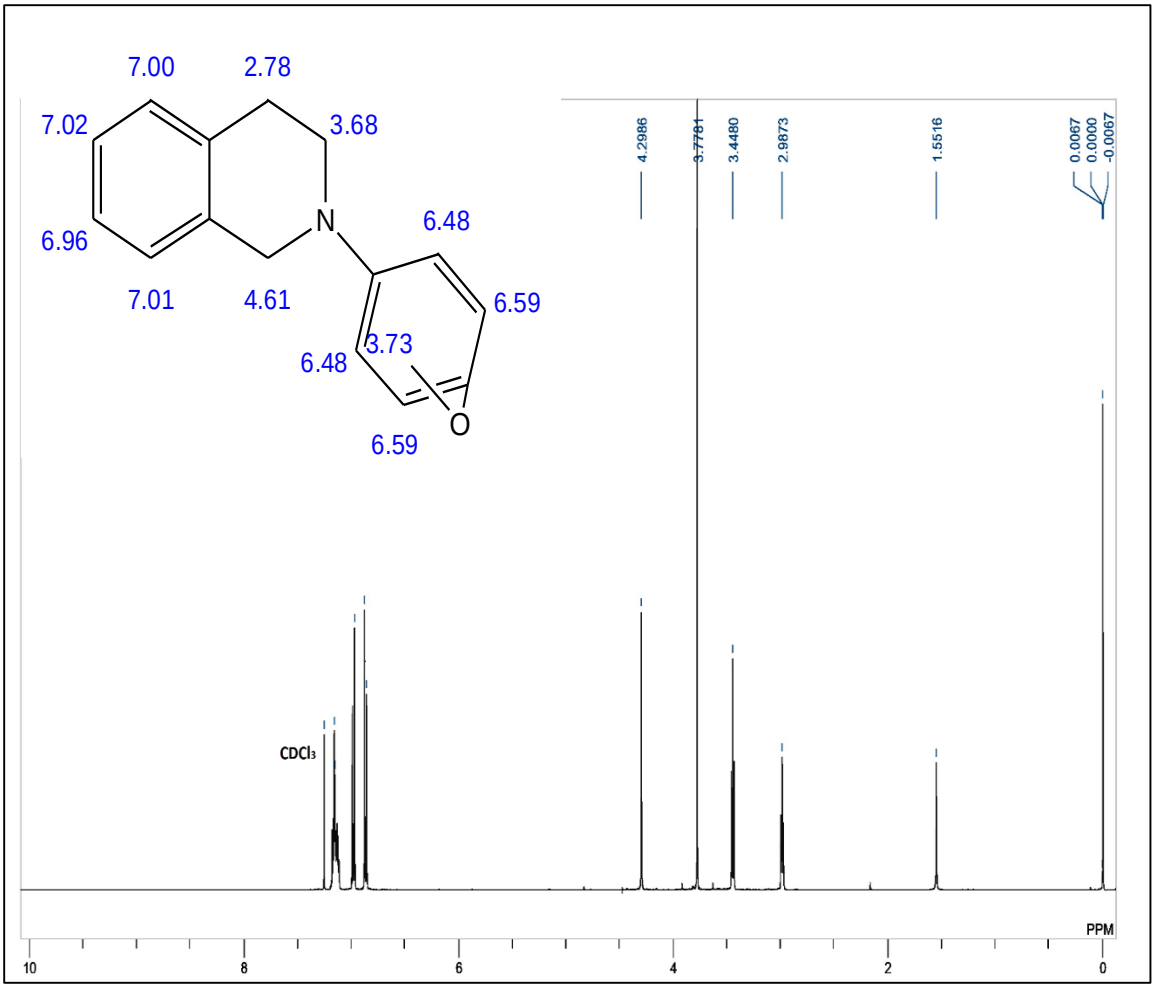
^{13}CNMR of Rose Bengal.



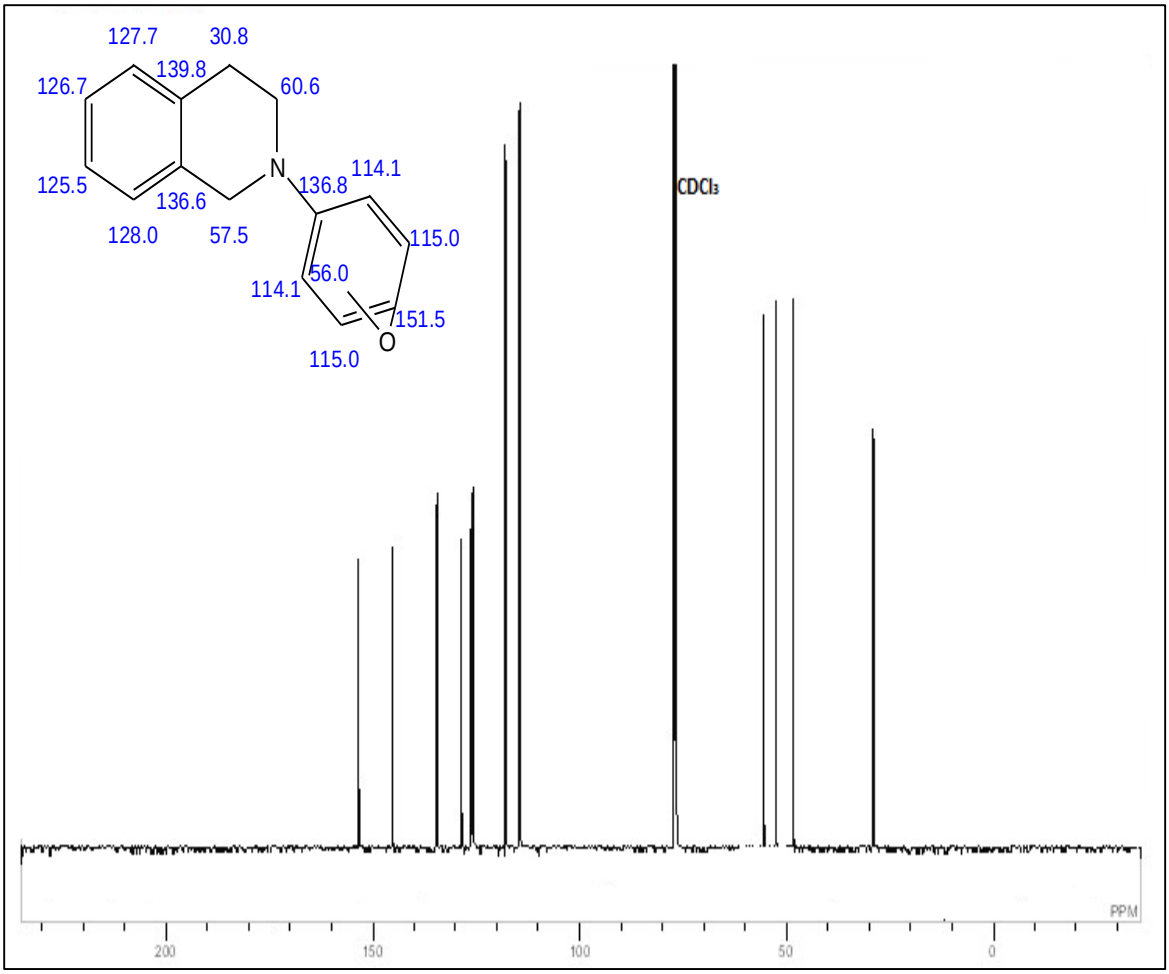
[1]HNMR of Eosin Y dye.



[13]CNMR of Eosin Y.

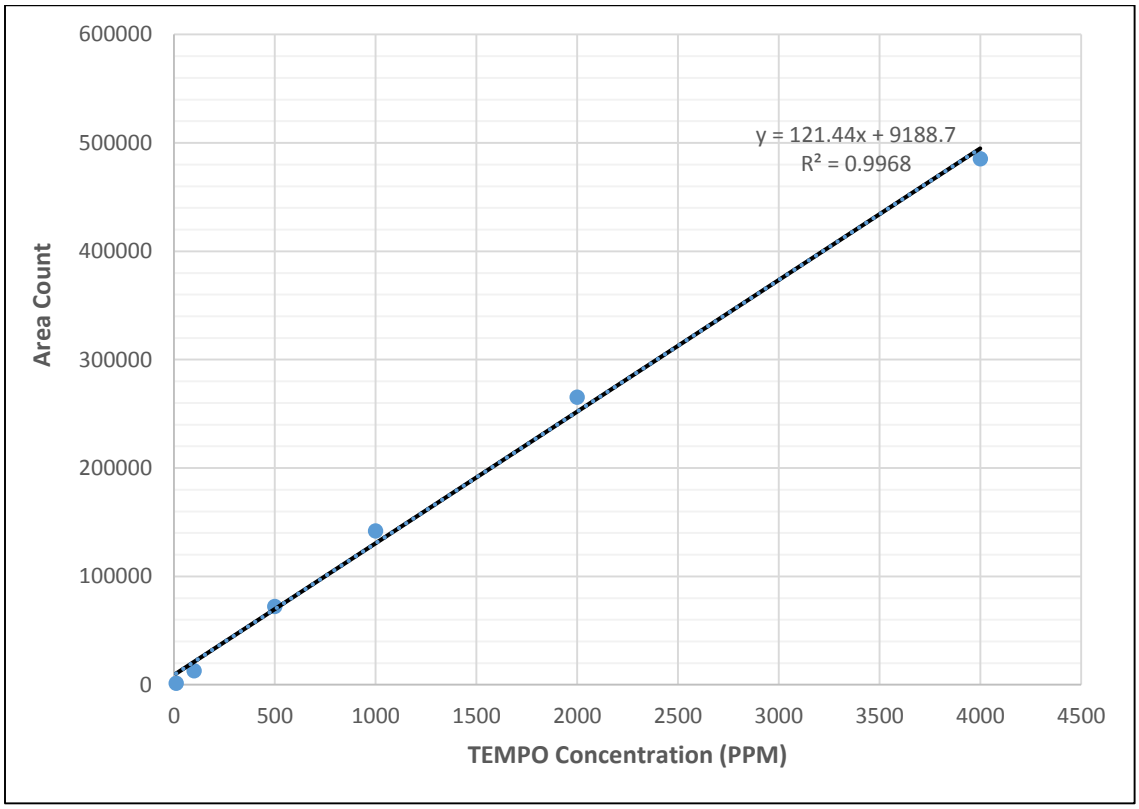


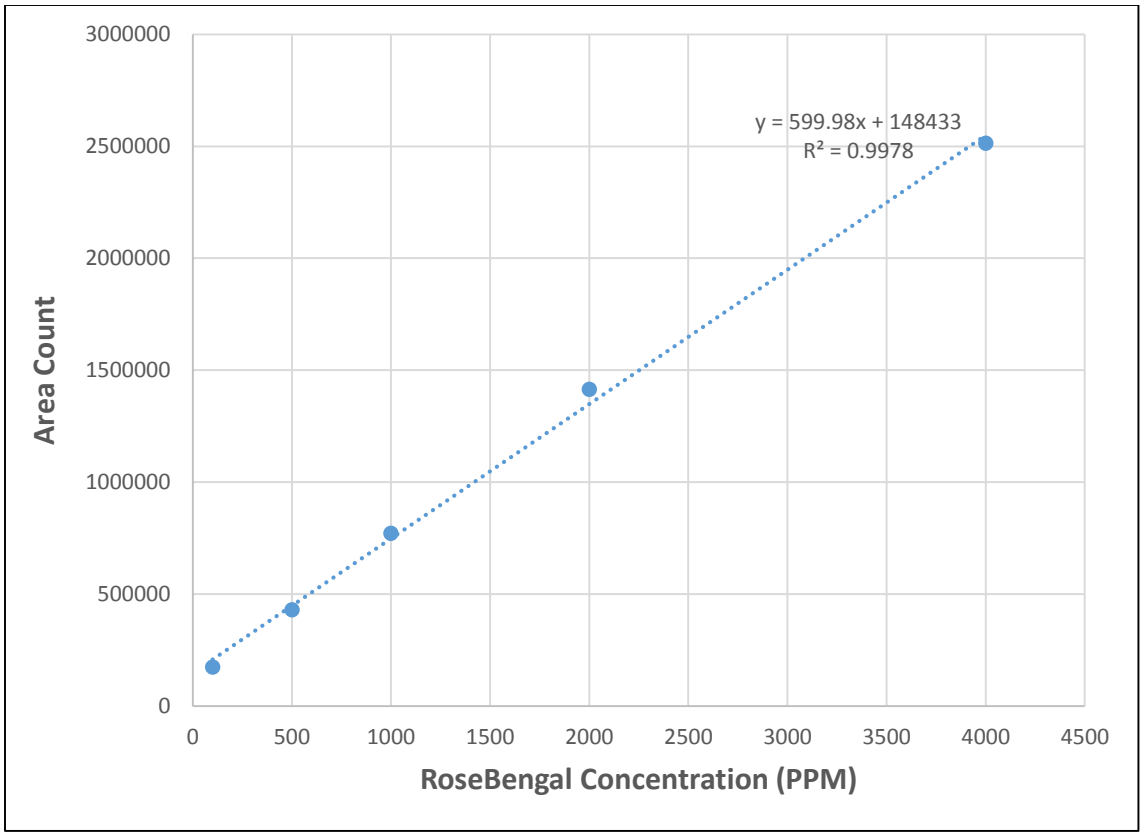
[1]HNMR of 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline.

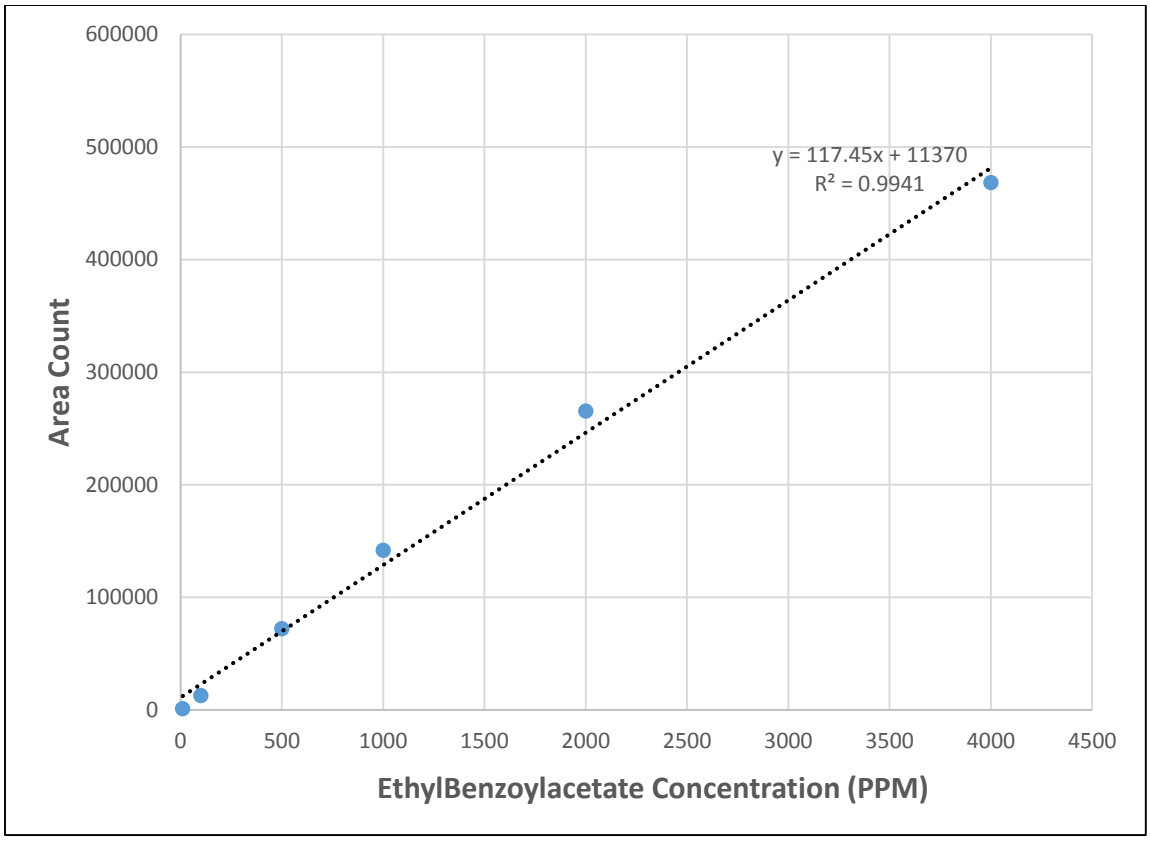


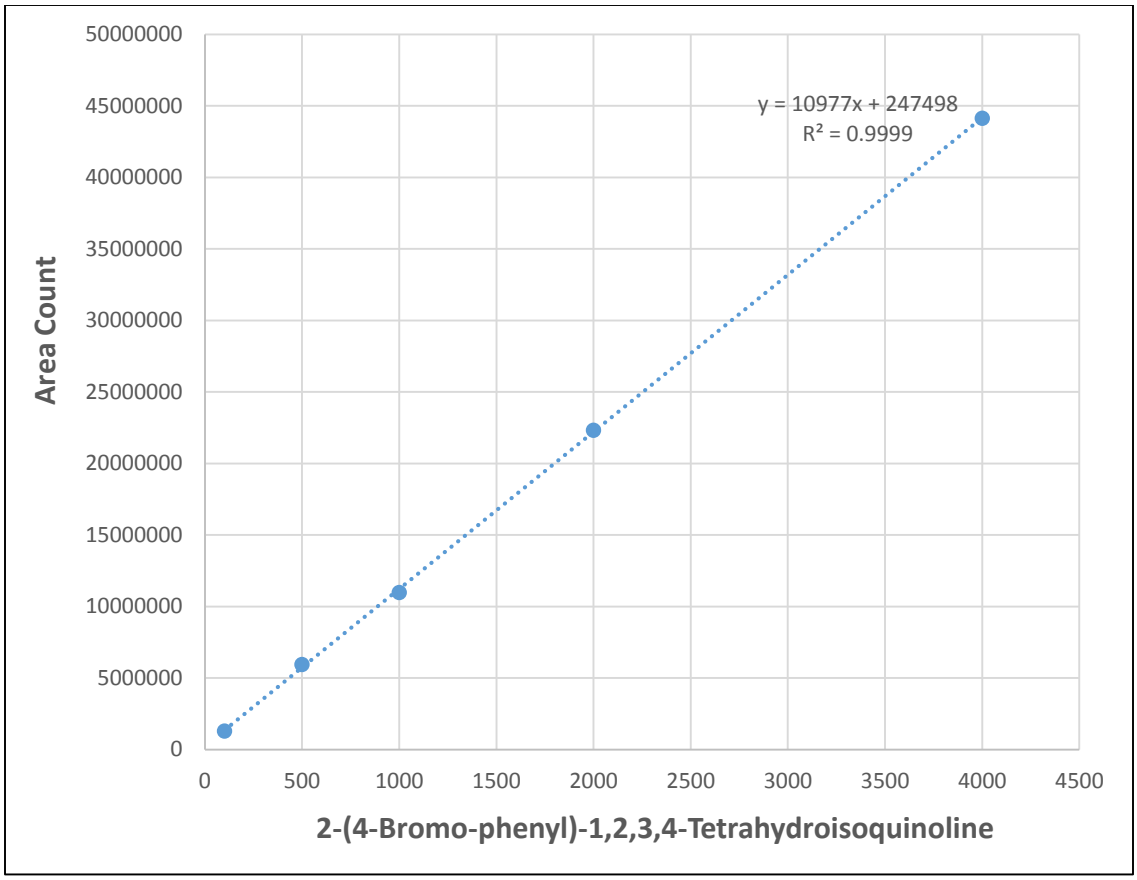
^{13}CNMR of 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline.

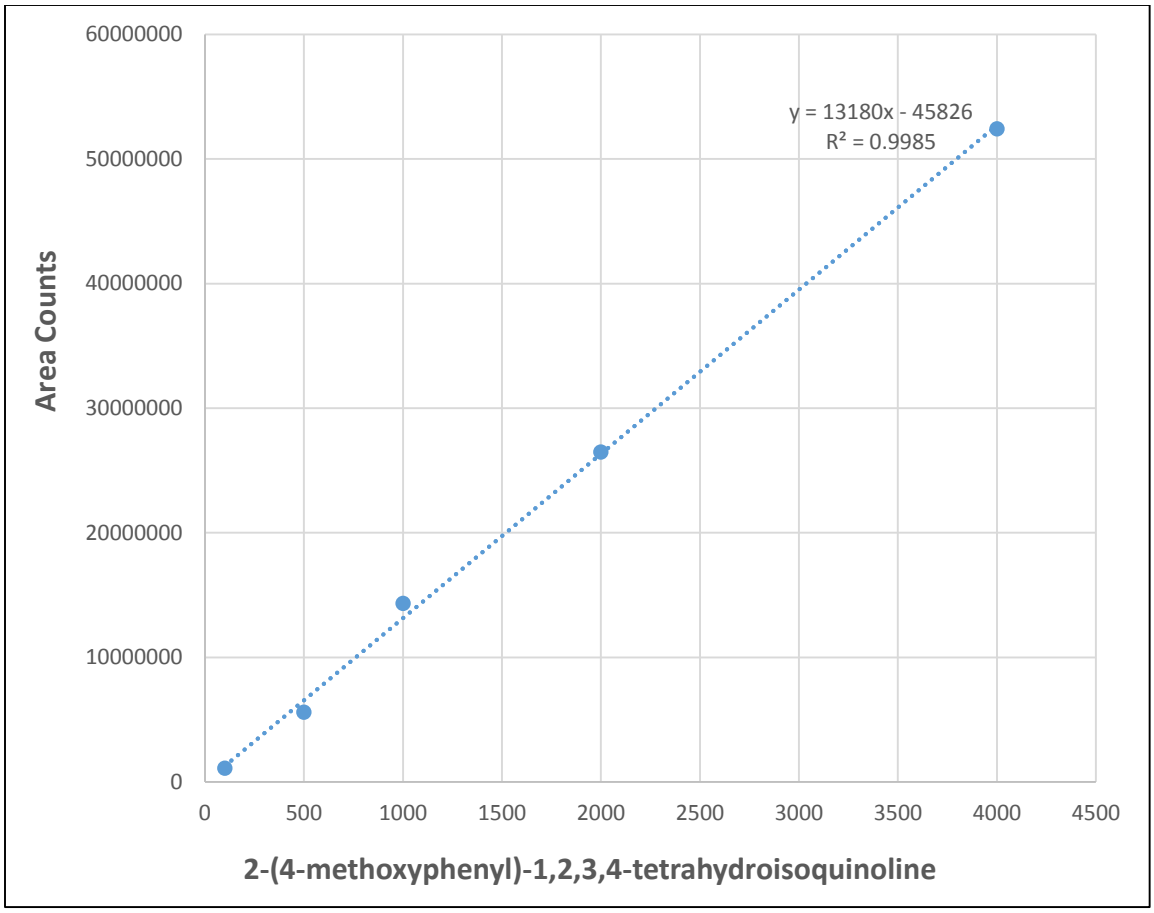
APPENDIX B: CALIBRATION CURVES

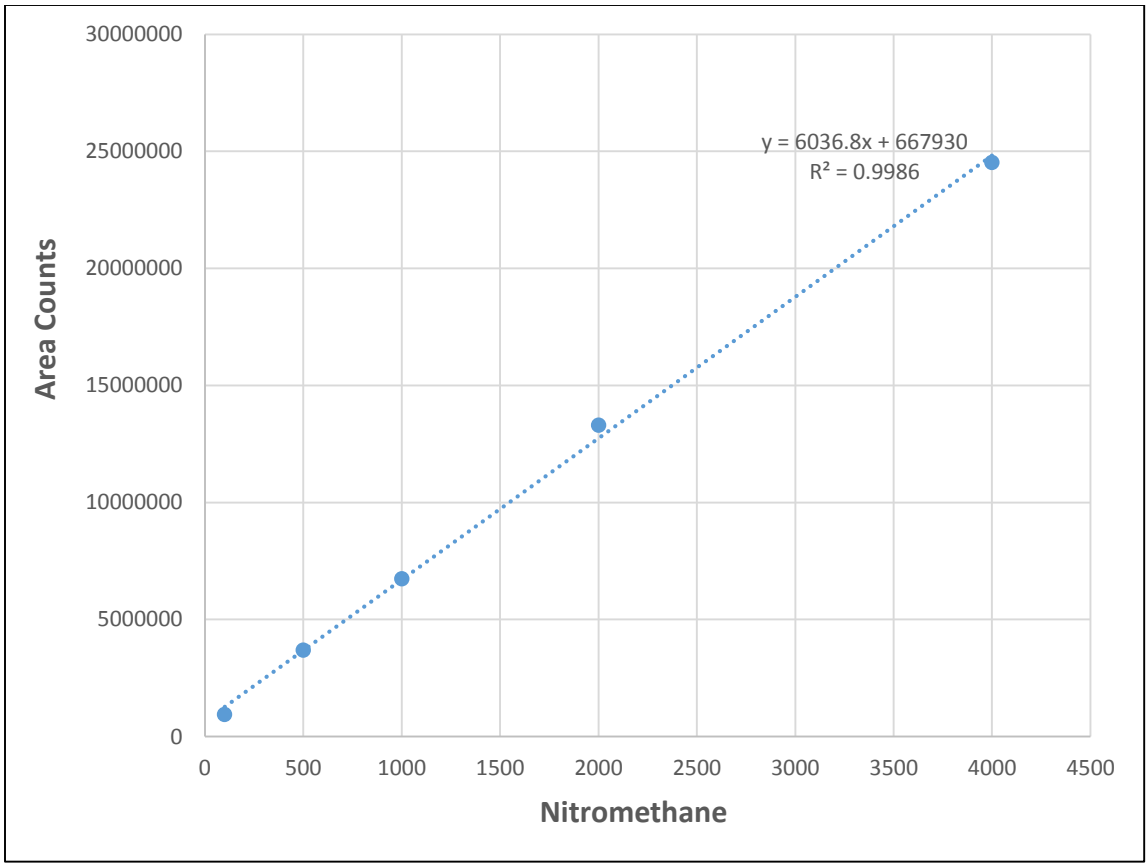


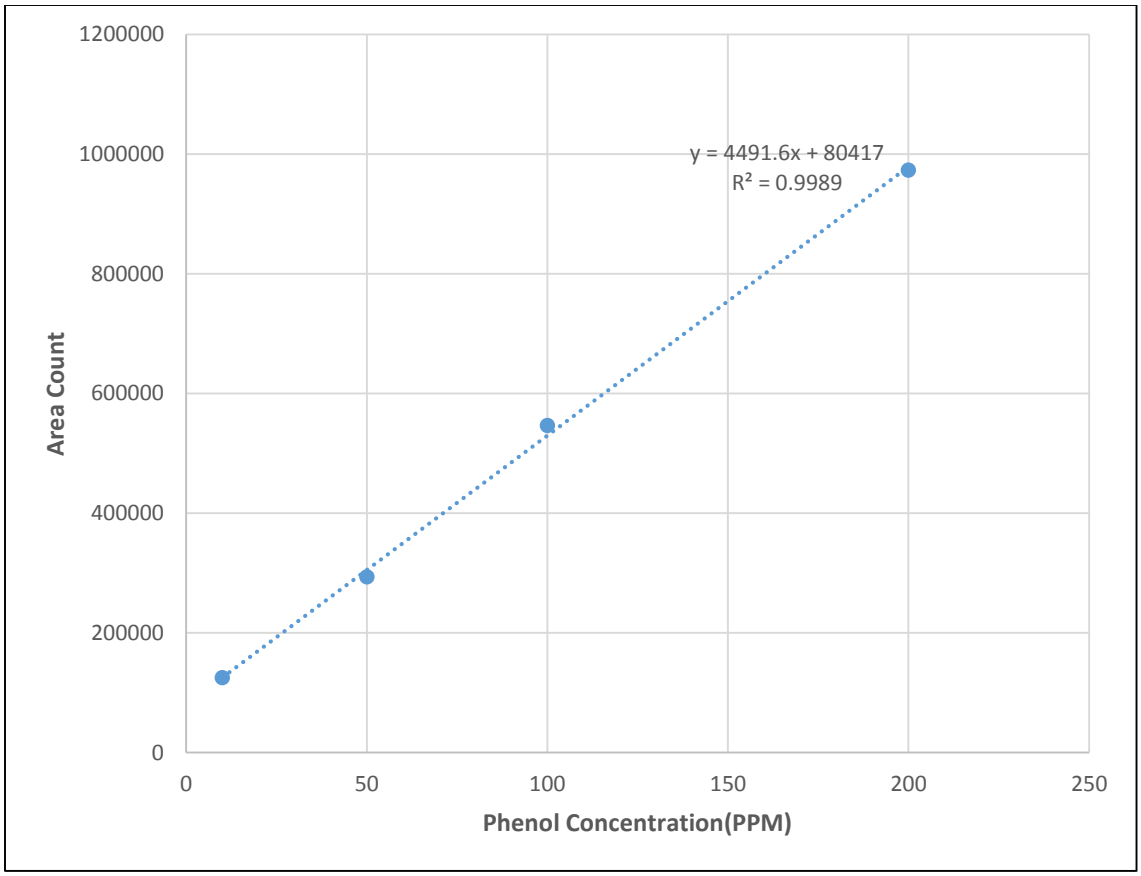

y = 599.98x + 148433
R² = 0.9978
Area Count
RoseBengal Concentration (PPM)
3000000
2500000
2000000
1500000
1000000
500000
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500


600000
500000
400000
300000
200000
100000
0
Area Count
y = 117.45x + 11370
R² = 0.9941
0
500
1000
1500
2000
2500
3000
3500
4000
4500
EthylBenzoylacetate Concentration (PPM)


y = 10977x + 247498
R² = 0.9999
Area Count
50000000
45000000
40000000
35000000
30000000
25000000
20000000
15000000
10000000
5000000
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500
2-(4-Bromo-phenyl)-1,2,3,4-Tetrahydroisoquinoline


60000000
50000000
40000000
30000000
20000000
10000000
0
Area Counts
y = 13180x - 45826
R² = 0.9985
0
500
1000
1500
2000
2500
3000
3500
4000
4500
2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline


30000000
25000000
20000000
15000000
10000000
5000000
0
Area Counts
y = 6036.8x + 667930
R² = 0.9986
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Nitromethane


1200000
1000000
800000
600000
400000
200000
0
Area Count
y = 4491.6x + 80417
R² = 0.9989
0
50
100
150
200
250
Phenol Concentration(PPM)

APPENDIX C: TABLES

Table showing Wavelengths (λ) nm of the dyes in different solvents used

Name of the Dye	**Wavelength (λ) nm**	**Solvent**
Fluorescein	450	Methanol
Rose Bengal	549	Water
Eosin Y	539	Methanol
Graphene Oxide	240	Water

REFERENCES

Akagawa, K., Fujiwara, T., Sakamoto, S., & Kudo, K. (2010). Efficient asymmetric alpha-oxyamination of aldehydes by resin-supported peptide catalyst in aqueous media. *Organic Letters*, *12*(8), 1804–7.

Akagawa, K., & Kudo, K. (2011). Peptide/laccase cocatalyzed asymmetric α-oxyamination of aldehydes. *Organic Letters*, *13*(13), 3498–501.

Alalm, M. G., Tawfik, A., & Chemicals, A. (2014). Solar Photocatalytic Degradation of Phenol in Aqueous Solutions Using Titanium Dioxide, *8*(2), 144–147.

Albini, A., & Fagnoni, M. (2004). Green chemistry and photochemistry were born at the same time Green Context, 1–6.

Albini, A., & Fagnoni, M. (2004). Green chemistry and photochemistry were born at the same time Green Context, 1–6.

Ansari, I. a, & Gree, R. (2002). TEMPO-catalyzed aerobic oxidation of alcohols to aldehydes and ketones in ionic liquid [bmim][PF6]. *Organic Letters*, *4*(9), 1507–9. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/11975615

Arora, R., Chanderia, K., Punjabi, P. B., & Sharma, V. K. (2010). Journal of Chemical and Pharmaceutical Research, *2*(2), 627–636.

Basheer, C., Jahir Hussain, F. S., Lee, H. K., & Valiyaveettil, S. (2004). Design of a capillary-microreactor for efficient Suzuki coupling reactions. *Tetrahedron Letters*, *45*(39), 7297–7300.

Basheer, C., Swaminathan, S., Lee, H. K., & Valiyaveettil, S. (2005). Development and application of a simple capillary-microreactor for oxidation of glucose with a porous gold catalyst. *Chemical Communications (Cambridge, England)*, (3), 409–10.

Bhunia, S. K., & Jana, N. R. (2014). Reduced Graphene Oxide-Silver Nanoparticle Composite as Visible Light Photocatalyst for Degradation of Colorless Endocrine Disruptors.

Bolm, C., Magnus, A., & Hildebrand, J. (2000). Catalytic synthesis of aldehydes and ketones under mild conditions using TEMPO/Oxone. *Organic Letters*, *2*(8), 1173–5. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/10804582

Brivio, M., Verboom, W., & Reinhoudt, D. N. (2006). Miniaturized continuous flow reaction vessels: influence on chemical reactions. *Lab on a Chip*, *6*(3), 329–44.

Brown, S. P., Brochu, M. P., Sinz, C. J., & MacMillan, D. W. C. (2003). The direct and enantioselective organocatalytic alpha-oxidation of aldehydes. *Journal of the American Chemical Society*, *125*(36), 10808–9.

Chauhan, A., & Saini, R. P. (2014). A review on Integrated Renewable Energy System based power generation for stand-alone applications: Configurations, storage options, sizing methodologies and control. *Renewable and Sustainable Energy Reviews*, *38*, 99–120.

Cheng, Z., Fu, F., Pang, Y., Tang, B., & Lu, J. (2015). Removal of phenol by acid-washed zero-valent aluminium in the presence of H2O2. *Chemical Engineering Journal*, *260*, 284–290.

Delville, M. M. E., Nieuwland, P. J., Janssen, P., Koch, K., van Hest, J. C. M., & Rutjes, F. P. J. T. (2011). Continuous flow azide formation: Optimization and scale-up. *Chemical Engineering Journal*, *167*(2-3), 556–559.

Divate, S. B., & Hinge, R. V. (2014). Review on Research Removal of Phenol from Wastewater by Using Different Methods, *4*(5), 5–7.

Esser, P., Pohlmann, B., & Scharf, H. (2009). The Photochemical Synthesis of Fine Chemicals with Sunlight, *2023*, 2009–2023.

Fernández, I., Renedo, C. J., Pérez, S. F., Ortiz, A., & Mañana, M. (2012). A review: Energy recovery in batch processes. *Renewable and Sustainable Energy Reviews*, *16*(4), 2260–2277.

Fletcher, P. D. I., Haswell, S. J., Pombo-villar, E., Warrington, B. H., Watts, P., Wong, Y. F., & Zhang, X. (2002). Micro reactors : principles and applications in organic synthesis, *58*(609), 4735–4757.

Francos, J., Borge, J., Díez, J., García-Garrido, S. E., & Cadierno, V. (2014). Easy entry to donor/acceptor butadiene dyes through a MW-assisted InCl3-catalyzed coupling of propargylic alcohols with indan-1,3-dione in water. *Catalysis Communications*, 1–5.

General Introduction to the chemistry of dyes. (1977) (pp. 55–67).

Gondal, M. a, Sayeed, M. N., & Seddigi, Z. (2008). Laser enhanced photo-catalytic removal of phenol from water using p-type NiO semiconductor catalyst. *Journal of Hazardous Materials*, *155*(1-2), 83–9.

Gou, B., Li, D., Yang, C., Xia, W., Li, Y., & Chen, X. (2012). Conversion of aryl CO to CC bond through a UV light activation/TEMPO oxidation cascade reaction. *Journal of Photochemistry and Photobiology A: Chemistry*, *233*, 46–49.

Hamza, A., J.T, F., Waziri, S. ., & Ajayi, O. . (2013). Solar photocatalytic degradation of phenol using nanosized ZnO and -Fe2O3. *Journal of Chemical Engineering and Materials Science*, *4*(7), 87–92.

Haswell, S. ., & P.watts. (2009). *Micro Process Engineering: A Comprehensive Handbook, Volume 1* (p. 1412). John Wiley & Sons. Retrieved from http://books.google.com/books?id=lWa6X7udAnIC&pgis=1

Hepbasli, A., & Alsuhaibani, Z. (2011). A key review on present status and future directions of solar energy studies and applications in Saudi Arabia. *Renewable and Sustainable Energy Reviews*, *15*(9), 5021–5050.

Ho, X.-H., Kang, M.-J., Kim, S.-J., Park, E. D., & Jang, H.-Y. (2011). Green organophotocatalysis. TiO2-induced enantioselective α-oxyamination of aldehydes. *Catalysis Science & Technology*, *1*(6), 923.

Hoffmann, N. (2008). Photochemical reactions as key steps in organic synthesis. *Chemical Reviews*, *108*(3), 1052–103.

Hsu, H.-C., Shown, I., Wei, H.-Y., Chang, Y.-C., Du, H.-Y., Lin, Y.-G., … Chen, K.-H. (2013). Graphene oxide as a promising photocatalyst for CO2 to methanol conversion. *Nanoscale*, *5*(1), 262–8.

http://www.imm.fraunhofer.de/en/about_us.html. (n.d.). Retrieved August 20, 2014, from http://www.imm.fraunhofer.de/en/about_us.html

Hu, R., Dai, S., Shao, D., Alsaedi, A., Ahmad, B., & Wang, X. (2015). Efficient removal of phenol and aniline from aqueous solutions using graphene oxide/polypyrrole composites. *Journal of Molecular Liquids*, *203*, 80–89.

Jakeway, S. C., de Mello, a J., & Russell, E. L. (2000). Miniaturized total analysis systems for biological analysis. *Fresenius' Journal of Analytical Chemistry*, *366*(6-7), 525–39. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/11225765

Jensen, K. F. (2001). Microreaction engineering * is small better ?, *56*, 293–303.

Journal, I., Energy, R., & Issn, E. E. (2014). Graphene Oxide Synthesized by using Modified Hummers Approach, *02*(01).

Kakhki, R. M., Nejati-Yazdinejad, M., & Kakeh, F. (2013). Extraction and determination of Rose Bengal in water samples by dispersive liquid–liquid microextraction coupled to UV–Vis spectrophotometry. *Arabian Journal of Chemistry*.

Kazmi, N. (2014). Solar Energy Potential in Saudi Arabia : A Geographic Information System (GIS) Based Study, 2032.

Krishnamoorthy, K., Mohan, R., & Kim, S.-J. (2011). Graphene oxide as a photocatalytic material. *Applied Physics Letters*, *98*(24), 244101.

Li, X., Zhang, J., Kang, S., Li, G., & Mu, J. (2014). Visible light photocatalytic activity of CuO/Cr2O3 co-loaded multiwalled carbon nanotubes sensitized with eosin Y for hydrogen evolution from water. *Ceramics International*, *40*(7), 10171–10176.

Li, Y., Pouliot, M., Vogler, T., Renaud, P., & Studer, A. (2012). α-Aminoxylation of ketones and β-chloro-α-aminoxylation of enones with TEMPO and chlorocatecholborane. *Organic Letters*, *14*(17), 4474–7.

Linden, S. M., & Necken, D. C. (1988). Bleaching Studies of Rose Bengal Onium Saltst, *13*(9), 1257–1260.

Liu Danadan, Xiu, Z., Liu, F., Wu, G., Adamson, D., Newell, C., … Alvarez, P. J. (2013). Perfluorooctanoic acid degradation in the presence of Fe(III) under natural sunlight. *Journal of Hazardous Materials*, *262*, 456–63.

Liu, H., Feng, W., Kee, C. W., Zhao, Y., Leow, D., Pan, Y., & Tan, C.-H. (2010). Organic dye photocatalyzed α-oxyamination through irradiation with visible light. *Green Chemistry*, *12*(6), 953.

Lo, H., & Ehrfeld, W. (1999). State-of-the-art in microreaction technology : concepts , manufacturing and applications, *44*, 3679–3689.

Luo, F., Yang, J., Li, Z., Xiang, H., & Zhou, X. (2015). Palladium-Catalyzed C-H Bond Acylation of Acetanilides with Benzylic Alcohols under Aqueous Conditions. *European Journal of Organic Chemistry*, n/a–n/a.

M, K., K S, R., Sivaraj, R., Kumar R T, R., & Abdul Salam, H. (2014). Photocatalytic degradation of endocrine disruptor Bisphenol-A in the presence of prepared CexZn1-xO nanocomposites under irradiation of sunlight. *Journal of Environmental Sciences (China)*, *26*(11), 2362–8.

Maleki, A., & Eslami, A. (2004). Potential of Rice Husk and Rice Husk Ash for Phenol Removal in Aqueous Systems Department of Environmental Health Engineering , Center for Environmental Research Tehran University of Medical Sciences , Tehran , Iran Department Environmental Health Enginee, *1*(4), 321–326.

Mang, J. Y., Kwon, D. G., & Kim, D. Y. (2009). Enantioselective α-hydrazination of α-fluoro-β-ketoesters catalyzed by chiral nickel complexes. *Journal of Fluorine Chemistry*, *130*(2), 259–262.

Markov, P., & Petkov, I. (1976). On the photosensitivity of dibenzoylmethane , benzoylacetone and ethyl benzoylacetate in solution, *33*, 1013–1015.

Mattay, J., & Griesbeck, A. G. (n.d.). Steps in Organic Synthesis.

Moulay, S. (2009). Towards water-borne organic synthesis : an education in chemistry, *18*, 1–21.

Moyo, M., Mutare, E., Chigondo, F., Nyamunda, B. C., Bag, P., Sciences, E., & Africa, S. (2012). Removal of phenol from aqueous solution by adsorption on yeast , saccharomyces cerevisiae, *11*(June), 486–494.

Narayanam, J. M. R., & Stephenson, C. R. J. (2011). Visible light photoredox catalysis: applications in organic synthesis. *Chemical Society Reviews*, *40*(1), 102–13.

Oelgemller, M., Jung, C., Ortner, J., Mattay, J., & Zimmermann, E. (2005). Green photochemistry: solar photooxygenations with medium concentrated sunlight. *Green Chemistry*, *7*(1), 35.

Oh, Y., Kim, S. M., & Kim, D. Y. (2009). Organocatalytic synthesis of quaternary stereocenter bearing a fluorine atom: enantioselective conjugate addition of α-fluoro-β-ketoesters to nitroalkenes. *Tetrahedron Letters*, *50*(32), 4674–4676.

Pan, Y., Kee, C. W., Chen, L., & Tan, C.-H. (2011). Dehydrogenative coupling reactions catalysed by Rose Bengal using visible light irradiation. *Green Chemistry*, *13*(10), 2682.

Pan, Y., Wang, S., Kee, C. W., Dubuisson, E., Yang, Y., Loh, K. P., & Tan, C.-H. (2011). Graphene oxide and Rose Bengal: oxidative C–H functionalisation of tertiary amines using visible light. *Green Chemistry*, *13*(12), 3341.

Pardeshi, S. K., & Patil, a. B. (2008). A simple route for photocatalytic degradation of phenol in aqueous zinc oxide suspension using solar energy. *Solar Energy*, *82*(8), 700–705.

PloughboyOrganic. (2013). *What are Organic Dyes and why are they Safer ?*

Pourahmad, A. (2013). Nanocomposite prepared from ZnS nanoparticles and molecular sieves nanoparticles by ion exchange method: characterization and its photocatalytic activity. *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy*, *103*, 193–8.

Protti, S., & Fagnoni, M. (2009). The sunny side of chemistry: green synthesis by solar light. *Photochemical & Photobiological Sciences : Official Journal of the European Photochemistry Association and the European Society for Photobiology*, *8*(11), 1499–516.

Raji Rathinavelu, J., & Palanivelu, K. (2014). Natural solar light driven degradation of refractory chlorophenolic pollutant using. *Journal of Environmental Chemical Engineering*, *2*(3), 1804–1812.

Ramamurthy, V. (1997). *Organic Photochemistry* (p. 608). CRC Press. Retrieved from http://books.google.com/books?id=rcNRSLe81LMC&pgis=1

Real, D., Johnston, R., Lauer, J., Schicho, A., & Hotz, N. (2014). Novel non-concentrating solar collector for intermediate-temperature energy capture. *Solar Energy*, *108*, 421–431.

Ren, X., Han, D., Chen, D., & Tang, F. (2007). Large-scale synthesis of hexagonal cone-shaped ZnO nanoparticles with a simple route and their application to photocatalytic degradation, *42*, 807–813. doi:10.1016/j.materresbull.2006.08.030

Roberge, D. M., Ducry, L., Bieler, N., Cretton, P., & Zimmermann, B. (2005). Microreactor Technology: A Revolution for the Fine Chemical and Pharmaceutical Industries? *Chemical Engineering & Technology*, *28*(3), 318–323.

Roth, B. H. D. (1989). The Beginnings of Organic Photochemistry, 1193–1207.

Roth, H. . (2000). *The Porphyrin Handbook: Synthesis and organic chemistry, Volume 1* (p. 405). Elsevier. Retrieved from http://books.google.com/books?id=MiVk6UhtgX8C&pgis=1

Roth, H. . (2004). *Synthetic Organic Photochemistry* (Vol. 30, p. 648). CRC Press. Retrieved from http://books.google.com/books?id=DnleWsWrDnMC&pgis=1

Saaby, S., Knudsen, R., & Ley, S. V. (2005). The Use of a Continuous Flow-Reactor Employing a Mixed Hydrogen- Liquid Flow Stream for the Efficient Reduction of Imines to Amines, 5–8.

Saeed, M., & Ilyas, M. (2013). Oxidative removal of phenol from water catalyzed by nickel hydroxide. *Applied Catalysis B: Environmental*, *129*, 247–254.

Sahin, A. Z., Aksakal, A., & Sunar, M. (1999). Solar-energy availability in the north-eastern Arabian peninsula, *64*, 323–329.

Sarria, V., Kenfack, S., Guillod, O., & Pulgarin, C. (2003). An innovative coupled solar-biological system at field pilot scale for the treatment of biorecalcitrant pollutants. *Journal of Photochemistry and Photobiology A: Chemistry*, *159*(1), 89–99. doi:10.1016/S1010-6030(03)00105-9

Services, H. (1996). Toxicology and carcinogenesis studies of acetonitrile in f344 / n rats and b6c3f , mice, (447).

Shamar, J. M. (2013). Determination of Some Phenols in Tigris River by HPLC, *26*(1), 250–258.

Sharma, S., Ameta, R., Malkani, R. K., & Ameta, S. (2013). Photocatalytic degradation of rose Bengal by semiconducting zinc sulphide used as a photocatalyst. *Journal of the Serbian Chemical Society*, *78*(6), 897–905.

Simon, L. M., Kotorman, M., Maraczi, K., & Laszlo, K. (2000). N -acetyl- L -arginine ethyl ester synthesis catalysed by bovine trypsin in organic media, 565–570.

Song, J., Yang, Y., Zhu, Y., & Jin, Z. (2013). A high precision tracking system based on a hybrid strategy designed for concentrated sunlight transmission via fibers. *Renewable Energy*, *57*, 12–19.

Stambouli, a. B. (2011). Fuel cells: The expectations for an environmental-friendly and sustainable source of energy. *Renewable and Sustainable Energy Reviews*, *15*(9), 4507–4520.

Stewart, A. J., Ridge, O., & Universities, A. (2008). Relevant Websites, (2), 2682–2689.

Straathof, N. J. W., Osch, D. J. G. P., Schouten, A., Wang, X., Schouten, J. C., Hessel, V., & Noël, T. (2014). Visible Light Photocatalytic Metal-Free Perfluoroalkylation of Heteroarenes in Continuous Flow. *Journal of Flow Chemistry*, *4*(1), 12–17.

Tahara, K., Mikuriya, K., Masuko, T., Kikuchi, J., & Hisaeda, Y. (2013). Dechlorination of DDT catalyzed by visible-light-driven system composed of vitamin B 12 derivative and Rhodamine B. *Journal of Porphyrins and Phthalocyanines*, *17*(01n02), 135–141.

Teplý, F. (2011). Photoredox catalysis by [Ru(bpy)3]2+ to trigger transformations of organic molecules. Organic synthesis using visible-light photocatalysis and its 20th century roots. *Collection of Czechoslovak Chemical Communications*, *76*(7), 859–917.

Tryba, B., Morawski, A. W., & Inagaki, M. (2003). Application of TiO 2 -mounted activated carbon to the removal of phenol from water, *41*, 427–433.

Vadivel, S., Vanitha, M., Muthukrishnaraj, a., & Balasubramanian, N. (2014). Graphene oxide–BiOBr composite material as highly efficient photocatalyst for degradation of methylene blue and rhodamine-B dyes. *Journal of Water Process Engineering*, *1*, 17–26.

Vasudevan, S. (2014). An efficient removal of phenol from water by peroxi-electrocoagulation processes. *Journal of Water Process Engineering*, *2*, 53–57.

Vértesi, a, & Simon, L. M. (1998). Carboxypeptidase A-catalyzed dipeptide synthesis in organic media. *Journal of Biotechnology*, *66*(1), 75–82. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/9866861

Wang, X., Liu, R., Jin, Y., & Liang, X. (2008). TEMPO/HCl/NaNO2 catalyst: a transition-metal-free approach to efficient aerobic oxidation of alcohols to aldehydes and ketones under mild conditions. *Chemistry (Weinheim an Der Bergstrasse, Germany)*, *14*(9), 2679–85.

Wiles, C., Watts, P., Haswell, S. J., & Pombo-villar, E. (2004). The Application of Microreactor Technology for the Synthesis of 1 , 2-Azoles Abstract :, (3), 7–11.

Wright, E., & Mcewen, E. (1952). Benzoylation of Ethyl Benzoylacetate in the Presence of Various Tertiary Amines ' BY PAUL, *1603*(6), 6–8.

Y.kikutani, A.Hibara, K.Uchiyama, H.Hisamoto, M.Tokeshi, & T.Kitamori. (2003). *Lab-on-a-Chip: Miniaturized Systems for (Bio)Chemical Analysis and Synthesis* (p. 402). Elsevier. Retrieved from http://books.google.com/books?id=8SouCxcRYBIC&pgis=1

Zhang, J., Wang, L., Liu, Q., Yang, Z., & Huang, Y. (2013). Synthesis of α,β-unsaturated carbonyl compounds via a visible-light-promoted organocatalytic aerobic oxidation. *Chemical Communications (Cambridge, England)*, *49*(99), 11662–4.

VITAE

Name : Ahmed Abdi Hassan

Nationality : Kenyan

Email : ahmeyow104@yahoo.com

Address : 365-7100 Garissa North Eastern Province Kenya

Academic Background : 2004 – 2008 University College of Education Zanzibar, affiliate college of International University of Africa (Sudan), Bachelor of Science Biology and Chemistry with Education.

2013 – 2015 King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, Saudi Arabia. Master of Science Degree – Environmental Science

Presentation : Hassan, A.A. "Design and Application of Glass Flow Capillary Reactor for α-Oxyamination, Dehydrogenative coupling and C-H Functionalization of Tertiary Amine Reactions Using Organic Dyes and Sunlight" 3rd International Laboratory Technology Conference & Exhibition. 28 – 30 October, 2014. Gulf Hotel, Kingdom of Bahrain. (Poster)

Experience : Research Assistant: Environment Laboratory, King Fahd University of Petroleum and Minerals, Department of Earth Science. Saudi Arabia. August 2013 – May 2015